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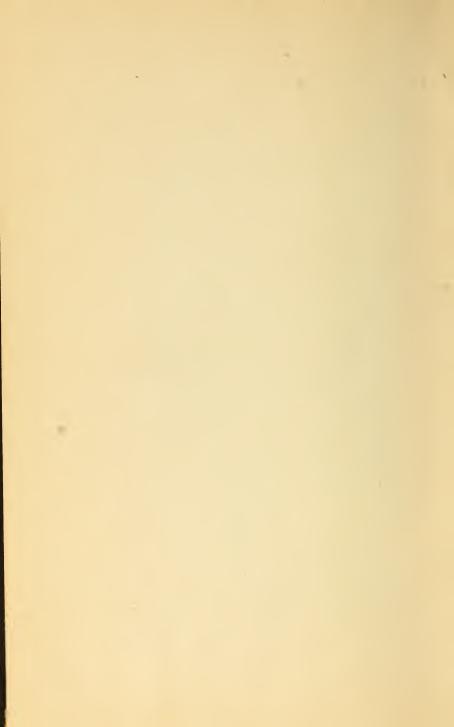
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Book 55

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# A STUDY COURSE IN ELEMENTARY CHEMISTRY

Prepared Especially for the Instruction and Training of Students of the American School

EUGENE E. GILL, Ph.D.

ASSOCIATE PROFESSOR OF GENERAL CHEMISTRY
ARMOUR INSTITUTE OF TECHNOLOGY

AND

B. B. FREUD, B.S., CH.E.

ASSOCIATE PROFESSOR OF ORGANIC CHEMISTRY
ARMOUR INSTITUTE OF TECHNOLOGY

AMERICAN SCHOOL

CHICAGO

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## A STUDY COURSE IN

#### ELEMENTARY CHEMISTRY

#### DIRECTIONS TO STUDENTS

Scope of book. This book is not to be taken as a complete text in elementary chemistry. It is frankly compiled for use with a textbook. In offering it, it is hoped that the lack of laboratory work may be compensated for by the frequent citation of chemical reactions which have an application in daily life and industry. The purpose has been to make this book, in so far as it is possible, take the place of class instruction. Little new subject matter has been introduced. Much repetition will be found. This was felt to be necessary to give proper emphasis to certain topics.

The course does not claim to be the full equivalent of the usual high school course in elementary chemistry where laboratory work accompanies the study of the textbook; it does, however, cover essentially the same topics. It is believed that a study of these pages in connection with the reading of the reference textbook will give the student such general knowledge of the principles of chemistry as will be useful in forming a part of his general education.

Method of using book. "An Elementary Study of Chemistry," second revised edition, by McPherson and Henderson, has been selected as the reference textbook; all references to pages occurring in this book refer to pages in McPherson and Henderson. Each of the twenty-five lessons assigns certain chapters in the textbook for study. These chapters should be read first, then the lesson in this study course studied, at the same time rereading those parts of the textbook that are referred to by pages. After careful study of the lesson and the corresponding chapters in McPherson and Henderson, the student should prepare the Exercises at the end of the lesson in this book, following the directions given in the note preceding the Exercises for Lesson I. The Exercises should be submitted for grading and correction after each five lessons.

#### LESSON I

#### MATTER AND ENERGY; VARIETIES OF MATTER

#### MATTER AND ENERGY

Assignment: "An Elementary Study of Chemistry," McPherson and Henderson, Chapter I

Science. Chemistry is a study of substances and their behavior toward other substances. It deals with the things with which we come in daily contact and thus has an important part in the understanding of the changes that take place in our daily lives. It is one of the natural sciences. Science may be defined as a study of the facts of nature, of the laws that state these facts, and the theories that explain the laws.

When men first began to observe the phenomena of nature as it existed and changed about them, only the one general subject of natural science was necessary to be considered, but soon the facts to be studied became so numerous that a division into branches of science was necessary. Today, to name only the most important sciences, we have botany, anatomy, geology, astronomy, chemistry, and physics.

Physics and chemistry. Of these sciences each one is more or less related to every other science. No one can be independent of the others, but we find that two, chemistry and physics, are much more intimately related than the others. These two are more fundamental as regards their subject matter. Botany deals with plants, anatomy with the animal body, geology with the earth's crust, astronomy with the heavenly bodies, but both chemistry and physics are more fundamental and study that which makes up these other bodies.

Matter. There are two fundamental things or ideas which we have to consider in studying the facts of nature. One is that to which we refer as matter. This composes all the things around us—chairs, books, our bodies, the earth, air, water, etc. The term matter is not easily defined. Matter is recognized by its properties, such as mass, inertia, impenetrability, etc. Of these, mass serves best to give a definition and matter may be said to be anything that has mass, or occupies space. This mass is usually deter-

mined by weighing the substance. Weight varies with altitude and latitude, mass does not. Therefore, weight is not a good definition of matter.

Energy. The other fundamental thing is energy. A little observation will show many examples of changes taking place in matter. Water freezes, wood burns, iron rusts, milk sours, alcohol evaporates, rocks disintegrate, animals and plants die and decay. The thing that brings about these changes in matter is called energy. Energy is sometimes defined as that which does work.

Changes in matter. A further study of these changes will show that they are of two kinds. If we take two wires, one made of platinum, the other made of magnesium, and hold each in a flame, we observe a difference in their behavior. Both give off light. The platinum retains its form and when removed from the flame returns to its original condition. It looks, feels, weighs, and measures the same. The magnesium wire, however, changes to a white powder and does not return to its original form and appearance. This white powder can be shown to weigh more than the original magnesium.

Physical changes. In the first case the platinum took back its original form when the original conditions returned. Such a change is an example of physical change. Other examples of physical change are freezing of water, melting of ice, moving of objects, dissolving of sugar. In all these cases it is noticed that the change is temporary and lasts only as long as the cause (high temperature in some cases) operates. The original properties return when this cause is removed. We learn to associate properties with the composition of matter. We may then say that a physical change is one that does not change the composition of matter. Physics is the science that studies physical changes.

Chemical changes. When the magnesium wire was heated, it underwent a permanent change. When the cause (heat) was removed, the matter did not return to its original form. A new substance was formed with a new set of properties. The metallic wire became a white powder which weighed more than the wire. This change in properties is associated with a change in the composition of the substance. Such a change is a chemical change and may be defined as a change in the composition of matter, recognized

by a permanent change in its properties. Chemistry is the study of chemical changes. The burning of fuels is the most common chemical change. The rusting of iron, souring of milk, explosion of gunpowder, digestion of food, fermentation of sugar, and disintegration of rocks are other chemical changes.

Conservation and transformation of energy. Energy exists in several forms, such as heat, electricity, mechanical energy, and light. These forms of energy can be converted into each other. The burning of coal gives heat, and this produces steam to run a steam engine, which may run a dynamo to give electricity, which in a light bulb gives light and heat (see illustration of energy transformation, page 7, McPherson and Henderson).

The question arises, in what form did the energy exist that gave the heat when the coal was burned? In the act of burning, the oxygen of the air and the carbon of the coal both undergo a chemical change. In this change heat energy is liberated. We say that this energy existed in the coal and the oxygen as chemical energy.

Every chemical change is accompanied by an energy change of some kind; energy is either given off or absorbed, usually as heat. Experience has taught us that energy cannot be created or destroyed but only transformed from one kind to another. This is stated as the law of the conservation of energy. A scientific law may be defined as a general statement of facts.

Conservation of matter. In all the changes which matter may undergo, it can be shown that there is neither loss nor gain in the amount of matter taking part in the change. As measured by weighing, it has been shown that the weights of all the products of a change are exactly equal to the weights of all the substances entering into the change. We may transform matter but cannot change its mass. This is known as the law of the conservation of matter and may be stated as follows: In any change to which matter is subjected, the mass remains the same.

One sometimes has to think a second time to see the truth of this in the case of burning fuels, where the ash left is obviously quite small compared to the mass of fuel used. If, however, weight of fuel plus weight of oxygen is compared with weight of ash plus weight of gaseous products formed, they will be found to be equal.

#### VARIETIES OF MATTER

#### Assignment: Chapter II, McPherson and Henderson

Classes of matter. From the point of view of its composition, matter may be divided into three classes, namely: elements, compounds, and mixtures. As illustrative of these classes, the experiments with iron and sulfur and with sugar should be studied (pages 13 and 14).

Heating either the iron or the sulfur without contact with the air would result in no chemical change. Intimately mixing them without heat still leaves them in a condition where all their individual properties are recognizable. Heating them together, however, produces a new substance with a set of properties of its own and differing from the original properties of iron and sulfur. The glow observed at the time of the action is due to heat liberated from the chemical energy existing in the iron and the sulfur. The action is exactly similar to the kindling of coal and oxygen, where the coal continues to burn after the fire is started.

Heating sugar, however, decomposes it into two new substances, carbon and water. Passing an electric current through water shows that it in time can be decomposed into two gases, oxygen and hydrogen.

Elements. The question arises, can these decompositions be carried farther? Continued trials convince us that hydrogen, oxygen, carbon, iron, and sulfur cannot be decomposed into other substances by any means now known. That is not saying that it is impossible to decompose them. Water was at one time thought to be undecomposable. Even in recent years it has been shown that some substances which were thought to be simple were in reality composed of two or more constituents.

Substances like those mentioned above are called elements. An element is a substance which has not as yet been decomposed into simpler substances. At present the number of known elements is between eighty and ninety.

Compounds. The iron sulfide formed when the iron and the sulfur were heated is a compound. Sugar and water, substances that can be decomposed into simpler substances, are compounds. This class of substances must be distinguished on the one hand from elements and on the other from mixtures.

This is not always easy, but the study of large numbers of substances shows that those that can be classed as compounds have a constant percentage composition. Thus, water is always found to contain 11.19 per cent hydrogen and 88.81 per cent oxygen.

A chemical compound is a substance composed of two or more elements in constant proportions, which elements have lost their original properties, the new substance having a set of properties of its own, and it cannot be separated into its elements by mechanical means.

Mixtures. The substance composed of iron and sulfur before it was heated is an example of a mixture. Sand and sugar shaken together would be a mixture. Ordinary concrete is another. The rock called granite is composed of three distinct substances which can be recognized by the naked eye: quartz, feldspar, and mica. All three are themselves well-known chemical compounds.

In all these instances, the substances can be separated into their constituent parts by mechanical means. The magnet separates iron from sulfur. Water would dissolve sugar from sand. Crushing the granite would make it possible to pick out the three kinds of rock. In these cases each constituent can be recognized by its individual properties, even while existing in the mixture. Further, the percentage amounts of the various constituents may vary, without radically changing the substance.

A mixture is a substance composed of two or more elements or compounds, in proportions that may vary, which still retain their original properties and can be separated from each other by mechanical means.

Chemical reactions. In the formation of compounds from the elements or in the decomposition of compounds into elements or simpler compounds, there is a considerable change in properties. Products are formed that are unlike the original substances.

Just as important as this, however, is the energy change that takes place. In every chemical change there is a transformation of energy. Chemical energy held in the substances is transformed into some other form, such as heat, and liberated; or heat, or other form of energy, is used and converted into chemical energy, which is held in the substances produced by the chemical change. This energy change is a necessary characteristic of every chemical change, or chemical reaction, as it is called. There is always a change in the composition of matter at the same time that the energy change occurs.

It is not possible to say what causes chemical changes. Energy change and matter change are simultaneous and neither can be said to be the cause of the other. To say that chemical affinity is the cause of chemical change tells us nothing because no one knows what causes chemical affinity. The expression simply means a chemical attraction, or tendency to combine.

It is important, however, to keep in mind that conditions have considerable influence in determining whether a reaction will or will not take place, and if it does take place, they determine its velocity. Applying heat or other forms of energy frequently promotes the speed of a reaction, either of combination or decomposition.

#### **EXERCISES\***

Read Carefully: Write out your answers to these questions. Place your name and full address at the head of the paper. Any cheap, light paper may be used; write on only one side of the paper. Do not crowd your work, but arrange it neatly and make it legible. Do not copy the answers; use your own words so that we may be sure you understand the subject.

- 1. State the meaning of science, matter, energy, scientific law.
- 2. Name and define two kinds of changes in matter.
- 3. Define chemistry and physics.
- 4. Give a number of examples of physical and chemical changes.
- 5. Name all the forms of energy.
- 6. Describe an experiment showing their transformation.
- 7. State the laws of conservation of energy and of matter.
- 8. Describe an experiment showing the formation of a compound of iron and sulfur.
  - 9. Define element, compound, and mixture.
  - $10. \quad Discuss the \ nature \ of \ chemical \ reactions \ and \ conditions \ influencing \ them.$
  - 11. Explain free, or native, state. What is a calorie?
  - 12. Describe the decomposition of water.
  - 13. Give the experiment of Lavoisier.
- 14. How could you show that the substances formed in burning a candle weigh more than the candle? What does this show?
  - 15. Solve problems 15 and 16, page 11, McPherson and Henderson.
  - 16. Answer questions 1, 3, 4, 5, 9, and 10, pages 10 and 11.
  - 17. Answer questions 1, 6, 10, 11, 12, and 13, pages 22 and 23.

<sup>\*</sup>Prepare this set of Exercises and hold it until those for Lessons II, III, IV, and V are also prepared and then send all five sets to the School.

#### LESSON II

#### **OXYGEN**

Assignment: Chapter III, McPherson and Henderson

Importance. The study of chemistry is first of all a study of substances. Of these it is natural to study the simple ones, that is, the elements, before taking up the compounds. In connection with the study of each elementary substance, its compounds will be considered. Of the elements, oxygen is by far the most important and is therefore studied first. Oxygen occurs in greater quantities than any other element. It occurs in the air as an element. In combination with other elements it is found in water, all forms of living matter, and the crust of the earth.

Oxygen is the active constituent of the atmosphere in which we live and is essential to all animal life. It also supports all the burning of fuels which supplies heat. All chemical changes that take place in nature, as well as the vast majority of those that are carried out in our laboratories and industrial plants, take place in an atmosphere of oxygen. The possible effect of the action of oxygen on the materials involved in these changes must be taken into account. So it is well at the beginning of our study to learn as much as we can of the properties and chemical behavior of oxygen.

Discovery. It was the discovery of oxygen as a constituent of the air which would support life and the burning of fuels more vigorously than air itself would that started the development of modern chemistry. Priestly and Scheele made the discovery at about the same time. It was Priestly who performed the experiments with mice, finding that a mouse could not live in air from which all oxygen had been removed and that in pure oxygen the mouse's activities were so vigorous that the animal soon died of exhaustion.

However, it was Lavoisier who recognized the exact nature of the substance and who gave it the name "oxygen." It was thought by Lavoisier that all acids contained oxygen, being formed by the addition of water to the oxides of non-metallic elements. Hence, he called the element oxygen, which means acid producer. He proved that the burning of metals resulted in an increase of weight by an amount equal to the loss in weight on the part of the air (see page 4.). This experiment established the relation of oxygen to that most important chemical change—combustion, or burning—as well as successfully combated the older theory of phlogiston.

**Preparation.** In the preparation of oxygen we must look to its natural sources, air, water, and other compounds containing it.

- 1. Obtaining oxygen from air. Air is a mixture of oxygen and nitrogen, both of which gases can be liquefied; but the resulting liquids have different boiling points (see "Liquid air," pages 108 and 141). If air is liquefied, the nitrogen boils off first, as it has the lower boiling point. Oxygen will be left. Oxygen obtained in this way is not pure, but it is pure enough for many commercial purposes. A large amount of oxygen for such uses is prepared in this way.
- 2. Obtaining oxygen from water. Passing an electric current through water which has a little sulfuric acid dissolved in it gives two gases, oxygen and hydrogen. This action is sometimes called the *electrolysis* of water (pages 16 and 17). The method gives quite pure oxygen and is used for its preparation on a large scale when purity is desired. By a similar action oxygen gas is liberated at one of the poles in certain electroplating processes.
- 3. Obtaining oxygen from various compounds. Heating certain compounds that contain oxygen will cause it to be liberated; not all compounds containing oxygen will give it up when heated. A few that yield oxygen when heated are mercuric oxide, potassium chlorate, sodium peroxide, and potassium nitrate. A common method for making oxygen on a small scale is to heat potassium chlorate. This gives oxygen and a compound of potassium and chlorine. This action works faster and at a lower temperature if some manganese dioxide is added, although just what part the manganese dioxide plays is not known, as no change can be noted in it when the action is complete, and as much of it remains as was used in the beginning. A substance used to change the velocity of an action, without apparently taking any part in it, is called a catalytic agent. Other examples of catalytic agents will be met with later.

Priestly obtained his oxygen by heating mercuric oxide, a red powder containing mercury and oxygen. This method is slow and expensive. Sodium peroxide when treated with water will yield oxygen and a compound known as sodium hydroxide. This is a good quick method to make the element. Examples of compounds which will not liberate oxygen when heated, though they contain considerable quantities of it, are copper oxide, calcium carbonate (or limestone), iron oxide, sugar, alcohol, sand, and carbon dioxide.

Properties. The physical properties and the chemical properties of substances must always be studied. The latter are sometimes referred to as chemical conduct. Even though we are studying chemical changes, it is necessary to know the physical properties of the substances we are dealing with. We cannot see a chemical change, and it is only possible to know that one has taken place by recognizing that we have obtained a substance with a new set of physical properties. Six important physical properties should be considered for every substance studied. They, in general, correspond to the common physical senses. They are physical state, taste, color, odor, density, and solubility.

Oxygen is a tasteless, colorless, odorless gas which can be liquefied. It is slightly heavier than air and slightly soluble in water. When liquefied, it boils at  $-182.9^{\circ}$  C. at atmospheric pressure.

Chemical conduct. The chemical conduct of oxygen as a supporter of burning, or combustion, is apparent. This, however, is only a part of its general tendency to combine with other elements or with compounds. The ordinary fuels are organic substances containing carbon and hydrogen. Oxygen will combine with these elements to form carbon dioxide and water, respectively. Oxygen will combine by direct addition with nearly all the elements. Of the eighty some elements known, only thirteen do not combine directly with oxygen. Gold, silver, and platinum are among these thirteen. By indirect methods oxygen compounds can be made with five of this group of thirteen. This fact emphasizes the wide range of its activity.

Its action is usually not very vigorous at ordinary temperatures. At such temperatures it does combine with a few elements like sodium and phosphorus with a fair velocity, but the action is made very rapid by raising the temperature. Usually a rather high temperature is necessary to cause appreciable union of oxygen with other substances. In the ignition of a match the necessary heat to ignite the phosphorus or phosphorus compound used is generated by friction, the oxygen being supplied by some compound like potassium chlorate. In old-fashioned gunpowder the combustion consists of the carbon and sulfur of the mixture combining with oxygen supplied by potassium nitrate.

Compounds formed by the union of oxygen with another element are called *oxides*. The union of oxygen with another substance is called *oxidation*. A substance that supplies the oxygen is called an *oxidizing agent*. Oxidation may be of two kinds, slow and rapid. The products of the action are the same in both cases and the total heat given off is the same in both.

However, if the oxidation is rapid enough, the heat will be intense enough to produce light. This is called *combustion*. In many cases combustion reactions are carried out for the heat they generate and not for the products they form. This is the case in all burning of fuel. The temperature at which light is given off, or combustion commences, is called the *kindling temperature*.

Uses of oxygen. Free oxygen is essential to the life of all animals except a few very low forms. Water animals obtain oxygen from the air that is dissolved in the water. Oxygen is used in the decay of waste organic matter, the decaying substance being oxidized into harmless gaseous substances. Certain forms of bacterial life are necessary to cause this oxidation to take place.

An example of purification by oxidation is the method sometimes used for sewage. The sewage is sprayed into the air (see page 34), and bacteria and oxygen destroy the harmful organic matter. Oxygen is utilized in some industrial processes and in laboratory work. Pure oxygen is used in the treatment of certain lung diseases where the patient cannot inhale enough air to support life.

Law of definite composition. In all the chemical changes that have been discussed in this and the previous lesson, it must be remembered that the change has always been between certain fixed weights of the various constituents if a compound is formed; or, if a compound is decomposed, it is always found to contain exactly the same percentages of its elements. The law of definite

composition may be stated as follows: The composition of a chemical compound never varies. This is true no matter where the compound may be found, nor does the manner of its preparation make any difference in its percentage composition.

#### **EXERCISES**

- 1. Relate the facts connected with the discovery of oxygen.
- 2. Describe the method for making pure oxygen on a commercial scale.
- 3. If oxygen on a large scale, but not pure, is required, how is it obtained?
- 4. Name several compounds that will yield oxygen when heated. Name several that will not.
- 5. What is meant by catalysis? Name a catalytic agent and the circumstances of its use.
  - 6. Give the physical properties of oxygen.
  - 7. Discuss the chemical conduct of oxygen.
  - 8. Define oxide, oxidation, combustion, and kindling temperature.
- 9. What is meant by heat of oxidation and combustion? Are they the same? Why?
  - 10. Explain spontaneous combustion. Give examples.
  - 11. Name the uses of oxygen.
  - 12. State the law of definite composition. Illustrate with examples.
  - 13. Solve problems 12, 13, 14, 15, and 16, pages 36 and 37.
  - 14. Answer questions 1, 2, 7, 8, and 10, page 36.

#### LESSON III

#### HYDROGEN; GAS LAWS

#### **HYDROGEN**

#### Assignment: Chapter IV, McPherson and Henderson

Discovery and occurrence. The study of hydrogen is second in importance only to that of oxygen because it, with oxygen, forms our most important chemical compound, water. It was isolated from water by Cavendish, and for that reason called hydrogen, meaning to produce water. Hydrogen does not occur in the elementary form in nature unless in rare traces. In the combined state it is found in water and in that large class of compounds called organic, which are the chief constituents of the bodies of all plants and animals. It is a constituent of sugar, starch, petroleum, natural gas, acids, and bases.

**Preparation.** 1. Electrolysis of water. Hydrogen is prepared from water by the use of the electric current. This method was studied under oxygen.

- 2. Action of certain metals on water. Some metals like sodium and potassium will liberate hydrogen from water at ordinary temperatures, forming at the same time compounds known as sodium or potassium hydroxides. These compounds belong to the class called bases and in their impure form are, respectively, the soda and potash lyes in common household use. In this preparation of hydrogen much heat is evolved and sometimes this will be sufficient to set fire to the hydrogen gas as it is evolved. Other metals, like iron and zinc, will liberate hydrogen from water only at high temperatures. Under these conditions the oxides of the metals are formed. Such metals as copper and silver will not set hydrogen free from water under any conditions.
- 3. Action of certain metals on acids. This is the usual laboratory method for making hydrogen. The metal used must be of such a nature as to be able to replace hydrogen from the acid. Iron and zinc are very suitable for this purpose, but copper and silver would not do at all. Theoretically, any acid might be used, but some acids are so weak that the evolution of hydrogen would be too slow to serve the purpose, while, in the case of other acids, secondary reactions take place that use up the hydrogen as fast as it is formed. For practical purposes, then, hydrochloric and sulfuric acids are the common ones used in the preparation of hydrogen. In the use of zinc and hydrochloric acid, the products of the action are hydrogen and zinc chloride. Iron and sulfuric acid give hydrogen and iron sulfate. For commercial uses hydrogen is made from water by using the electric current, or by using steam and iron.
- 4. Water gas as source of hydrogen. There has recently come into use a method of obtaining hydrogen for commercial purposes from water gas. This gas is made by passing steam over hot carbon in the form of coke or anthracite coal and consists of a mixture of hydrogen and carbon monoxide. Water gas is frequently used for fuel and illuminating purposes. Hydrogen can be obtained from it by liquefying the carbon monoxide. Hydrogen for balloon uses was made in this way during the European War.

Properties and chemical conduct. Hydrogen is the lightest of all the elements, being 15.88 times lighter than oxygen. Because of its lightness, it is much used to fill balloons. When pure, it is an odorless, colorless, and tasteless gas. It is slightly soluble in water. It can be liquefied and solidified. A remarkable property of hydrogen is its ability to be absorbed, or occluded, by metals—in most cases in traces, but gold, platinum, and palladium occlude large volumes of it.

In its chemical conduct it is much less active than oxygen With some elements under proper conditions it forms compounds called hydrides. It will combine with oxygen, chlorine, nitrogen, and sulfur quite readily. With oxygen and chlorine it forms explosive mixtures which are dangerous if not handled carefully. In working with hydrogen it is necessary to prevent its mixing with air, for dangerous explosions would occur if a flame came in contact with such a mixture. When oxygen and hydrogen as mixed in proper proportions and heated to 800 degrees, a violent explosion takes place. A jet of hydrogen gas will burn quietly in the air, forming water; the flame is almost colorless if free from impurities. By weight, 1 part of hydrogen combines with 7.94 parts of oxygen.

It is to be noted that chemically hydrogen is the opposite of oxygen. It does well the things oxygen does poorly and does not do the things oxygen does best. Oxygen combines with most of the metals, hydrogen does not; hydrogen combines with the non-metals, oxygen does so with less facility. For this reason it is usually said that hydrogen does not support combustion. In other words, it does not combine with the things that we have learned will burn in the air, that is, in oxygen.

Reduction. Hydrogen has so great a tendency to combine with oxygen that it will extract it from many of its compounds under suitable conditions. If we pass hydrogen over heated copper oxide, the oxygen will combine with hydrogen to form water and leave copper. The making of iron from iron oxide in a blast furnace is a similar reaction in which carbon takes the place of hydrogen. The oxide of the metal is reduced. Reduction is the removing of oxygen from a compound. The substance used to bring about this reduction is called a reducing agent.

Reduction and oxidation are opposite processes. The two processes take place together, one substance being reduced and the other oxidized. Later it will be shown that these terms can be used to include elements with properties similar to oxygen and hydrogen.

#### GAS LAWS

#### Assignment: Chapter V, McPherson and Henderson

Volume of gases. We are all familiar with the variation in volume of gases under different conditions of pressure and temperature. Toy balloons and rubber tires show this. The gas in them contracts under outside pressure and expands with increase temperature, sometimes causing blowouts. Quantities of gases are measured more conveniently by volume than by weighing. But, since the volume varies with conditions, the measured volume must be corrected to a standard set of conditions for pressure and temperature according to the laws of expansion and contraction.

The law of Boyle. The law of Boyle states the rule for volume change when the pressure changes and other conditions remain unchanged: The volume of a given mass of any gas varies inversely as the pressure, the temperature remaining constant. Thus, if a gas measures 500 cc. under a certain pressure, it will measure 1000 cc. if the pressure is halved, or 250 cc. if the pressure is doubled. This law may be expressed by a formula by letting  $P_1$  and  $P_2$  represent the two pressures and  $V_1$  and  $V_2$  the two volumes. Then

$$V_1:V_2::P_2:P_1$$

which may be written

$$\frac{V_1}{V_2} = \frac{P_2}{P_1}$$

or

$$V_1 P_1 = V_2 P_2$$

Standard pressure. We must have a unit of measurement for pressure as we have a yardstick to measure length or a pound to measure weight. For pressure, the pressure of the atmosphere at sea level is chosen. The weight of this column of air will support a column of water, of equal cross-sectional area, 1033.3 cm. in height. Since 1 gm. of water measures 1 cc., a

column of water 1 sq. cm. in cross-sectional area and 1033.3 cm. high weighs 1033.3 gms., and a column of air of the same cross-sectional area weighs the same.

The column of water is too long for convenient use so its value is expressed in terms of a denser liquid, mercury. Mercury is 13.59 times as dense as water. Divide 1033.3 cm. by 13.59 and we have 76 cm. as the height of the column of mercury which one atmosphere will support. This is usually read as 760 mm., and standard pressure is equal to that exerted by a column of mercury 760 mm. in height.

Example. Suppose oxygen is measured as 500 cc. at a pressure of 730 mm. What will its volume be at 760 mm.?

According to Boyle's law,  $V_1: V_2:: P_2: P_1$ , 500 cc. and 730 mm. are the first conditions, and the unknown volume X, and 760 mm., the second conditions. Substitute these in the formula and we have

500: X:: 760: 730

Solving

$$760X = 500 \times 730$$
$$X = \frac{500 \times 730}{760} = 480.26 \text{ cc.}$$

Absolute temperature. A study of the expansion of gases for temperature changes shows that there is an increase in volume of  $\frac{1}{273}$  of the volume at 0° C. for every degree centigrade the temperature is raised. Correspondingly there is a decrease of  $\frac{1}{273}$  of the volume at zero centigrade for every degree it is lowered.

If the temperature were lowered 273° below zero, the given mass of gas would occupy no volume. This is impossible, but all known gases become liquids before reaching this point. Theoretically -273° C. becomes the temperature of no volume, and this temperature is therefore the absolute zero. A thermometer constructed with this point as zero would measure absolute degrees of temperature. A comparison of these degrees with the volume of a gas would show them to be directly proportional.

The law of Gay-Lussac. The above facts may be stated as follows: The pressure remaining constant, the volume of a given mass of any gas will vary directly as the absolute temperature. This is called the law of Gay-Lussac. It may be expressed in formulas as follows:

 $V_1:V_2::T_1:T_2$ 

or

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

or

$$V_1 T_2 = V_2 T_1$$

Example. Five liters (5000 cc.) of hydrogen are measured at 27° C. What will its volume be at 7° C.?

In solving a problem of this nature it is always necessary to change the temperatures which are given in centigrade degrees to absolute degrees by adding 273 to the temperature given. Using the formula  $V_1: V_2:: T_1: T_2$  and substituting the appropriate values for the letters, we have

5000: X:: (27+273): (7+273)

Solving

$$300X = 1400000$$
  
 $X = 4666.67$  cc.

If both temperature and pressure changes are to be corrected for, the result in one case is to be used as the given value in the second correction, and each part of the problem solved as shown above.

Example. What will a given quantity of a gas measure at 37° C. and 700 mm. pressure, if it measures 500 cc. at standard conditions? Standard conditions are 0° C. and 760 mm. pressure.

We may correct for pressure first, applying the formula of Boyle's law,  $V_1: V_2:: P_2: P_1$ .

Substituting we have

500: X:: 700: 760

Then

$$X = \frac{500 \times 760}{700} = 542.8$$
 cc.

This value now becomes the given volume to be corrected for temperature according to the law of Gay-Lussac, which is represented by the following formula:  $V_1: V_2:: T_1: T_2$ Substituting we have

$$542.8: X:: 273: (273+37)$$
  
 $X = \frac{542.8 \times 310}{273} = 616.3 \text{ cc.}$ 

Therefore 616.3 cc. is the volume occupied by the gas at 37° C. and 700 mm. pressure.

The Kinetic theory. The gas laws just studied are experimental facts. But why do all gases behave in such a regular manner? An attempt to explain the facts as stated by a law is called a theory. These laws are explained by what is known as

the kinetic theory. The word "kinetic" means motion. It is supposed that all gases are composed of many small moving particles. These are called molecules. The molecules are far apart, hence the compressibility of gases. They are moving in straight lines with great velocities, striking each other and the sides of the containing vessel; this accounts for the pressure the gas exerts and its tendency to expand. Heat increases the velocity and therefore causes the expansion.

Assuming equal weight for all the molecules of the same gas but different weights for molecules of different gases, the kinetic theory suggests that equal volumes of all gases, the temperature and pressure remaining the same, contain the same number of molecules since they exert equal pressure. This statement is known as Avogadro's hypothesis and will be referred to in Lesson XVI.

#### **EXERCISES**

- 1. Describe three methods for making hydrogen.
- 2. State the physical properties of hydrogen.
- 3. Discuss the chemical conduct of hydrogen.
- 4. Define reduction and give two examples.
- 5. Explain why hydrogen sometimes explodes.
- 6. What are hydrides? Name four.
- 7. Solve problems 3, 12, 13, 14, and 15, page 51.
- 8. State the law of Boyle; of Gay-Lussac.
- 9. Discuss the selection of a standard pressure.
- 10. What is absolute zero? How is this point selected?
- 11. State the kinetic theory and Avogadro's hypothesis.
- 12. Solve problems 6, 7, 8, 9, and 10, pages 62 and 63.
- 13. Answer questions 2, 4, 5, 9, and 10, page 51.
- 14. Answer questions 1, 2, 3, 4, and 5, page 62.

#### LESSON IV

#### WATER; THREE STATES OF MATTER

#### Assignment: Chapters VI and IX, McPherson and Henderson

Occurrence. Water is certainly the most important compound we have to study. It occurs in greater quantity than any other. As the most widely used solvent it makes possible the occurrence of large numbers of chemical changes. It is necessary to the growth of plants and the digestion of food by animals. Its

industrial uses are numerous. From a scientific point of view it is one of our most stable substances and a determination of its composition is the starting point in developing the theories of chemistry. Besides occurring on the earth's surface, it is found as a part of many substances. All plant and animal bodies contain it—nearly 70 per cent of the human body is water. Most foods contain a large amount of water and some mineral bodies are found to contain it, such as blue vitriol and gypsum.

Impurities in water. Natural waters contain two kinds of impurities. They are mineral and organic.

As the water travels over or through the earth it dissolves a portion of the solid matter with which it comes in contact. These mineral substances are usually common salt and compounds of calcium, magnesium, and iron. Since these substances prevent the formation of a lather with soap, such waters are called hard; water which lathers well contains little mineral matter and is called soft. These impurities do not make the water unfit to drink, unless present in very large amounts. They are harmful for industrial uses such as in laundries and boilers. In the latter case they form boiler scale. A more complete discussion of hard water and boiler scale will be given in Lesson XXI.

Organic impurities found in water consist of substances formed by the decay of vegetable and animal matter, substances found in sewage, and forms of living microörganisms which usually accompany such products.

Effect of organic matter upon health. The effect of the organic matter present upon the health is very small. The harm is caused by the microörganisms, or bacteria, which are disease producing. Bacteria are forms of plant life. Not all bacteria produce disease; many kinds are not only harmless but useful, if not necessary, to human life; but some kinds produce serious diseases, such as tuberculosis, pneumonia, measles, smallpox, typhoid fever.

As an example, take typhoid fever. This is a disease of the small intestine. It is here that the typhoid bacteria lodge and carry on their life processes, resulting in the fever. This disease can only be acquired by taking these bacteria into the alimentary canal by means of the mouth. This means that our food and

drink must contain the germs of the disease. The typhoid bacteria pass from the person suffering with the disease in the bowel excrement. Sewage containing this excrement may mix with the water supply, rendering it unfit to drink. Flies are also guilty of acting as carriers. They go from sewage deposits to food supplies and carry the bacteria on their feet.

Detection of impurities. Mineral matter is detected by evaporation and analysis of the residue. Organic matter is detected by a sanitary analysis which shows the presence not only of organic matter itself but also of nitrogen compounds that result from the decay of organic matter. Sodium chloride always accompanies sewage, so its presence is significant. Large amounts of these substances make the water suspicious.

A bacterial examination for typhoid bacteria is not practical. To be safe we would have to examine every drink of water. We must assure ourselves that the water is safe from contamination with sewage. A bacterial test to show this is made for colon bacteria, which are always present in the large intestine in great numbers and, therefore, always found in sewage.

Purification of water. Distillation of water is the most effective way of purifying water. In this method the water boils and the steam condenses. The result is pure water. Solid matter is left behind. For most industrial purposes this is too costly, but it is used by the chemist and druggist. Artificial ice is made from distilled water.

For drinking purposes boiling the water and allowing it to cool renders it safe. The heat kills the bacteria but does not remove the dissolved matter. On a large scale water is purified by cities by methods of filtration. Slow sand filters and so-called mechanical filters are used.

Properties of water. When pure, water is colorless (except that it has a bluish tinge in thick layers), odorless, and tasteless. The temperatures of boiling, freezing, and greatest density are important. These are 100°, 0° and 4° C., respectively. A remarkable, and very useful property, is its ability to dissolve other substances. Such solutions are employed by chemists in studying the action of substances, since action is more rapid in solution.

Water is a very stable substance; that is, it is hard to decompose. Heated to 2500° C., only a small amount is decomposed into its elements. Its decomposition by means of the electric current is an indirect action. Water holds its oxygen firmly and is not a good oxidizing agent; however, carbon and some metals, as iron, will take the oxygen and set free hydrogen. In this way an illuminating gas is made from carbon and steam.

Water forms hydrates with many compounds by combining directly with them. The water in hydrates is called water of hydration. Such water is in a state of chemical combination with the rest of the substance, as is shown by the fact that the percentage composition is constant. For example, blue vitriol is a hydrate of copper sulfate and always contains exactly 36.03 per cent of water. Water in this state of chemical union can be easily removed from the compound by heating slightly above the boiling point of water. This shows that the chemical union is very weak compared with that between the elements in ordinary compounds, such as copper oxide, carbon dioxide, and even mercury oxide.

Composition of water. The quantitative composition of water can be shown by methods of analysis or synthesis. Synthesis means building up from smaller parts. In analysis water is decomposed, as with the electric current, and the amounts of hydrogen and oxygen determined. In general, this shows 2 volumes of hydrogen to 1 of oxygen or, by weight, 1 part of hydrogen to nearly 8 parts of oxygen. The method is not very accurate.

Synthetic methods are more accurate. Two of these have been used. That of Berzelius and Dumas was first used. It consists of passing hydrogen over hot copper oxide, with absorption tubes to collect and weigh the water formed. The loss in weight of the copper oxide is the weight of oxygen used. The weight of the water minus the weight of the oxygen gives the weight of the hydrogen. The method of Morley is more accurate. He used the eudiometer. This is filled with a mixture of hydrogen and oxygen which is exploded by the electric spark. The volumes of hydrogen and oxygen entering into the action can be calculated as weights. Morley's experiments gave a result of 1 part by weight of hydrogen combining with 7.94 parts by weight of oxygen. This value is very important and should be remembered.

If this experiment is carried out at ordinary temperatures, the product of the action is water in liquid form and its volume is insignificant. If, however, the eudiometer is surrounded by a steam jacket to keep the temperature at the boiling point, we find that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam. This value should be remembered, as use will be made of it later. The student should here read the experiments described on pages 74–79 inclusive.

Hydrogen peroxide. Hydrogen and oxygen form another compound besides water. This compound contains 15.88 parts by weight of oxygen in combination with 1 part of hydrogen. Hence it is called hydrogen dioxide sometimes, which means twice as much oxygen as in water. It is not made by direct union of the elements. Barium peroxide and sulfuric acid will react to form barium sulfate and hydrogen peroxide. The barium sulfate is insoluble and may be filtered off, leaving a solution of hydrogen peroxide.

Pure hydrogen peroxide is hard to obtain and is very unstable, breaking down with explosive violence into water and oxygen. Catalytic agents increase the speed of this decomposition. Because it gives off its extra oxygen easily, it is a good oxidizing agent. As such it is used as an antiseptic and bleaching agent; it oxidizes certain colored compounds and will bleach hair and some dyes.

Law of multiple proportions. Considering the compounds hydrogen peroxide and water, we see that two elements may unite to form two compounds, but that they do so in different proportions. It is further observed that the quantity of oxygen which unites with a fixed weight of hydrogen is exactly twice as much in one case as in the other. Many other examples of the same kind could be named. These facts may be stated as the law of multiple proportions as follows: When two elements combine to form two or more compounds there is always a small whole-number ratio between the several weights of one element which are in combination with a fixed weight of the other. This is the fourth law of chemical combination stated thus far. The fifth will be discussed in the next lesson.

States of matter. We have learned that water exists as a solid, liquid, and gas. These states are known as the physical

states of matter. Many other kinds of matter can exist in all three states. All gases have been liquefied and solidified, but all solids have not been liquefied or vaporized. A change from one state to another is a physical and not a chemical change.

Liquids evaporate at all temperatures but the evaporation is more rapid as the temperature rises. The vapor thus formed exerts a pressure. This pressure is called the vapor pressure of the liquid. When this pressure is equal to the atmospheric pressure, the change to the gaseous state is rapid. A change in the atmospheric pressure would change the temperature at which the vapor pressure would overcome the atmospheric pressure. The boiling point of a liquid is defined as the temperature at which the vapor pressure just exceeds the atmospheric pressure. At this point a certain amount of heat will be used up to change the liquid to a gas. This is known as the heat of vaporization. For water, 539 calories are required to change 1 gram of liquid to 1 gram of vapor at the boiling point.

Ozone. A form of matter is known which can be shown to contain only oxygen but which has properties quite different from those of oxygen. The main difference is that ozone is much more active and has a much higher energy content. It changes to oxygen; consequently it acts as a very powerful oxidizing agent. It is a bleaching agent, and it destroys many low forms of life and is therefore used as a disinfectant for purifying water and air.

It can be prepared by passing a silent electric discharge through oxygen. Energy is thus stored up in the ozone as chemical energy. Several forms of an element differing only in the chemical energy they contain are said to be *allotropic* forms of that element. Graphite and diamond are allotropic forms of carbon.

#### **EXERCISES**

- 1. Discuss the occurrence and uses of water.
- 2. What are the kinds of impurities in water? State the harm each does.
- 3. How are these impurities detected?
- 4. Discuss the methods for purifying water.
- 5. State the properties of water.
- 6. Give the weight composition and the volume composition of water. What volume of steam would be formed from 2 volumes of hydrogen?
  - 7. Describe methods by which this composition can be determined.

- 8. State composition, preparation, properties, and uses of hydrogen peroxide.
  - 9. State the law of multiple proportions and give an example of it.
- 10. What is meant by vapor pressure of a liquid, boiling point, heat of vaporization, allotropic?
  - 11. State the composition, preparation, properties, and uses of ozone.
  - 12. Solve problems 14, 15, 16, and 17, page 115.
  - 13. Solve problems 12, 13, 14, 15, and 16, page 85.
  - 14. Answer questions 1, 2, 4, 5, 6, and 7, page 84.
  - 15. Answer questions 2, 3, 4, 6, 7, 10, 11, 12, and 13, page 115.

#### LESSON V

### ATOMIC THEORY; EQUATIONS ATOMIC THEORY

#### Assignment: Chapter VII, McPherson and Henderson

Law of combining weights. Of the laws previously studied three deal with the weight relations in chemical change. These are (1) the law of conservation of matter, (2) the law of definite composition, and (3) the law of multiple proportion. The law of combining weights is the fourth. These four laws are the fundamental laws of weight relations in chemical change.

In the study of water it was found that 1 gm. of hydrogen combined with 7.94 gms. of oxygen. This compound and its composition furnish the most satisfactory numerical relation to use for a starting point in studying other numerical relations. If we study calcium oxide, we find that 7.94 gms. of oxygen combine with 19.88 gms. of calcium; 19.88 gms. of calcium combine with 16 gms. of sulfur. We may, by studying the composition of a large number of compounds of different elements, that is, by analyzing their compounds, make a list of the elements and assign a number to each element. Such number will represent the weight of the element to which it is assigned that will combine with the assigned weight values of the other elements. Using whole numbers for the values, a brief list is here given: H=1, O=8, Ca=20, S=16, K=39, Cl=35, Br=80, Na=23, I=127, Cu=63, F=19, Zn=65.

The student must keep in mind that these numbers are experimentally determined and are facts beyond question. Not every element in the above list will combine with every other, but

where they do not combine they will take the place of each other in compounds in weight proportions corresponding to the above numbers. Thus, hydrogen does not combine with zinc, but in their compounds with chlorine 1 gm. of hydrogen will be equivalent to 65 gms. of zinc. These weights are called *combining*, or equivalent, weights.

The standard. These numbers are only relative and, for the above list, are the weights found to combine with or be equivalent to 1 gm. of hydrogen. They are relative to hydrogen. Any other element could be taken as a standard for comparison and any number assigned to it. The ratio between the combining weights would not change though the numbers would be different if some other number was assigned to hydrogen.

As a matter of fact, oxygen is most commonly used as the standard, because more elements will combine with it than with hydrogen. If 1 gm. of hydrogen combines with 7.94 gms. of oxygen, then 1.008 gms. of hydrogen will combine with 8 gms. of oxygen. This last value is the one selected for a standard. The combining, or equivalent, weight of an element is then the weight of it, in grams, which will combine with 8 gms. of oxygen. Since some elements combine with oxygen in more than one proportion they have more than one combining weight. The numbers which represent the several combining weights of any element are always small whole-number multiples of the smallest combining weight (law of multiple proportion).

The law of combining weights is stated as follows: To each element may be assigned a number which in itself, or when multiplied by some small integer, expresses the weight by which the element combines with other elements.

Explanation demanded. These four laws state the facts of chemical union, but to the normal mind something is still lacking. Why this regular behavior? This question demands an answer. The law of multiple proportions, in particular, presses for an explanation. The answer must lie in the nature of matter. The answer given to this question by Dalton is the simplest and most satisfactory.

There are five oxides of nitrogen. With 7 gms. of nitrogen we find combined respectively 4, 8, 12, 16, and 20 gms. of oxygen.

Why always a whole-number multiple of 4, as 2, 3, 4, 5 times 4? Never do we have a fractional multiple, as 3.5 or 4.2. Does it not suggest to us, that the amount of oxygen represented by 4 parts by weight represents the unit of oxygen by which chemical action is taking place, and that in the other compounds we have 2, 3, 4, or 5 of these units? This is what Dalton thought when he stated the atomic theory.

Atomic theory. This theory suggests that the laws of chemical union are explained, if we assume that all elements are made up of small unit particles, which we call atoms. The atom is defined as the smallest particle of an element that can take part in chemical changes of that element. All the atoms of each element have the same weight, but atoms of different elements have different weights. When two or more elements unite to form a chemical compound, it requires a definite number of atoms of each element; hence, a compound always has the same composition. The weight of the atoms do not change in chemical change because there is no gain nor loss in total weight.

If two elements form more than one compound, it is because one, two, three, or four atoms of one element combine with a fixed number of atoms of the other element; thus establishing the small whole-number ratio between the weights of one element which combine with a fixed weight of the other (multiple proportion).

If these atoms always have the same weight, then the numbers assigned as the combining weights of the elements, or some small multiple of them, can be taken to indicate the relative weights of the atoms themselves. These, then, are the atomic weights. The actual weights of the atoms cannot be determined. We must use their relative weights as referred to some one of the elements as a standard. Oxygen is the most satisfactory to use as a standard. The ratio of hydrogen to oxygen in water is the fundamental ratio.

It will be shown in Lesson XVI that water contains two atoms of hydrogen and one of oxygen. We must either use 0.5 as the atomic weight of hydrogen or double the numbers in the ratio 1.008 to 8 for the composition of water. If we do the latter, we have 2.016 to 16. The atomic weight of hydrogen can then be taken as 1.008 and that of oxygen as 16. This is the standard generally used.

Molecules. The atom is the smallest unit of matter that enters into chemical changes; the smallest unit that takes part in physical changes is called the molecule. There are molecules of elements as well as of compounds. Usually a molecule is composed of two or more atoms. The molecules of compounds are made up of the atoms of the elements composing them. The molecules of elements are made up of the atoms of the single element, frequently two or more, but some elements are known which contain but one atom in a molecule, for example, mercury.

#### **EQUATIONS**

#### Assignment: Chapter VIII, McPherson and Henderson

Formulas and percentage composition. The analysis of a compound is usually expressed in percentage, or parts per hundred. The chemist can express composition in terms of atomic weight quantities in the molecule, or the number of atoms of each element in the molecule of the compound. For this purpose the symbol of the element is used to represent one atomic weight of the element. Thus Hg stands for 200 parts by weight of mercury, and O for 16 parts by weight of oxygen. The compound mercuric oxide is represented by HgO. This is called a formula.

If we know the formula of a compound and the atomic weights of its elements, it is a simple problem to calculate the parts per hundred. If the atomic weight of mercury is 200 and that of oxygen is 16 and one atom of each combine to form a molecule of the compound, this molecule can be said to have a weight of 216 relative to our standard. Divide 200 by 216 and we have the per cent of mercury in the compound.

Determination of formulas. On the other hand, if we know the percentage composition and the atomic weights, we can calculate the number of atoms in a molecule of the compound, that is, determine its formula. To determine the actual molecular formula it is necessary that the molecular weight of the compound be known. It is not always possible to know this. We may still determine the formula that represents the smallest possible percentage composition of the compound. This is called the *empirical*, or experimental, formula.

Sulfuric acid contains 2.06 per cent H, 32.69 per cent S, and 65.25 per cent O, that is, that many grams in 100 gms. If we divide these numbers by the atomic weights of their elements, we will obtain the relative number of atoms of each element in the compound. These relative numbers are quite likely to be fractions, but atoms do not exist as fractions; they are present only in whole quantities. Keep in mind that the relative numbers of atoms are a ratio and their value can be changed by dividing by a common factor without changing the ratio. The simplest formula will be one that contains but one atom of at least one element. The relative numbers of the different kinds of atoms in the formula would be found by dividing the fractional values first obtained by the smallest of the lot. Thus:

$$2.06 \div 1.008 = 2.04 \\ 32.69 \div 32.06 = 1.02 \\ 65.25 \div 16 = 4.08 \\ \end{pmatrix} \div 1.02 = \begin{cases} 2 \\ 1 \\ 4 \end{cases}$$

Therefore sulfuric acid contains two atoms of hydrogen, one of sulfur and four of oxygen. This is written  $H_2SO_4$ . In a formula the number of atoms is represented by a small figure written slightly below the line and after the symbol to which it refers. The actual molecular formula may be some multiple of this, as  $H_4S_2O_8$  or  $H_6S_3O_{12}$ .

Facts expressed by formulas. Just as the symbol represents, not simply an abbreviation of the name of an element, but its atomic weight, so the formula of an element or compound shows more than simply the kind of elements in its composition. In addition to showing the number and kind of atoms in a molecule of a compound, the formula shows the relative weights of these atoms and the molecular, or formula, weight of the compound. Thus, H<sub>2</sub>SO<sub>4</sub> shows sulfuric acid to contain two atomic weights of hydrogen, one atomic weight of sulfur, and four atomic weights of oxygen. The weight of the molecule of sulfuric acid is, therefore,

$$(2 \times 1.008) + 32.06 + (4 \times 16) = 98.076$$

This is called the *molecular weight* because this weight represents the simplest composition of sulfuric acid.

In dealing with the substance we use grams or pounds. We do not know the gram weight of atoms. Since the atomic

weights are relative to each other, the ratio is the same, if we allow H to represent 1.008 gms. of hydrogen; S, 32.06 gms. of sulfur; O, 16 gms. of oxygen; and H<sub>2</sub>SO<sub>4</sub>, 98.076 gms. of sulfuric acid. These weights are called the *gram-atomic weights* for the elements and the *gram-molecular*, or formula, weights for the compounds.

Equations. A grouping together of the formulas of the substances entering into a reaction and those of the products formed and connecting the two groups by a convenient sign constitutes a chemical equation. Such an equation is not mathematical in its nature. It is simply a shorthand method of representing the facts of the chemical change which has taken place.

If experiment shows that 98 gms. of sulfuric acid will act with 65 gms. of zinc to give 161 gms. of zinc sulfate and 2 gms. of hydrogen, we can briefly express these facts by using the formulas that represent the weights of the compounds. Thus,

$$H_2SO_4+Zn\rightarrow ZnSO_4+H_2$$

Such an equation would be read as follows: One formula weight of sulfuric acid and one atomic weight of zinc react to give one formula weight of zinc sulfate and one formula weight of hydrogen. There are two atoms in the molecule of hydrogen.

In order to write an equation it is necessary to know certain facts about the chemistry of the reaction. Only then can you write the equation. In the above example it must be shown by experiment that 98 gms. of H<sub>2</sub>SO<sub>4</sub> react with 65 gms. of zinc to give 161 gms. of ZnSO<sub>4</sub> and 2 gms. of hydrogen. This experimental work is not possible for the beginning student. He must, however, get the same facts from the textbooks or an instructor.

Classes of equations. A study of chemical changes shows that practically all may be represented by four types of reactions:

1. Combination, in which two elements or compounds unite to form one compound:

$$2H_2 + O_2 \longrightarrow 2H_2O$$
  
 $2Hg + O_2 \longrightarrow 2HgO$   
Fe +S  $\longrightarrow$  FeS  
C +O<sub>2</sub>  $\longrightarrow$  CO<sub>2</sub>  
CaO + H<sub>2</sub>O  $\longrightarrow$  Ca(OH)<sub>2</sub>

2. Decomposition, in which a compound decomposes into simpler parts:

$$\begin{array}{cccc} 2KClO_3 & \longrightarrow 2KCl & +3O_2 \\ 2H_2O & \longrightarrow 2H_2 & +O_2 \\ CaCO_3 & \longrightarrow CaO & +CO_2 \\ 2HgO & \longrightarrow 2Hg & +O_2 \end{array}$$

3. Substitution, in which one element replaces another in a compound:

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$
  
 $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$   
 $Fe + 2HCl \longrightarrow FeCl_2 + H_2$ 

4. Double decomposition, in which two compounds react, the molecules of both decomposing and recombining to form two new compounds:

$$\begin{array}{lll} BaO_2 & +H_2SO_4 \longrightarrow BaSO_4 & +H_2O_2 \\ AgNO_3 + NaCl & \longrightarrow AgCl & +NaNO_3 \\ HCl & +NaOH \longrightarrow HOH & +NaCl \\ H_2SO_4 & +2NaCl \longrightarrow Na_2SO_4 + 2HCl \end{array}$$

Heat and conditions of a reaction. The above equations represent the products of the reaction and the proper quantities of each substance to complete the reaction, but they do not represent the energy change that always takes place. In many cases this energy change is a heat change. Heat is either absorbed or given off by the action. While the equations do not show this, the student must not forget that such a change is always occurring. Neither do the equations show the conditions under which the action will occur. These conditions are important, and the proper ones must be obtained to get the reaction.

The equation is a statement of the relative weights of the reacting substances in terms of their formula weights. If the equation correctly represents the facts of the reaction, the same ratio between the weights of the several substances holds good, no matter in what weight units they may be measured—grams, pounds, ounces, or what not. If we know the gram or pound weight of one substance involved in the reaction, we can use the ratio of relative weights shown by the formula weights in the equation to calculate the actual weights of the other substances concerned. The equation must always be written to show this relation before a start can be made to solve a problem.

Examples. How many grams of oxygen will be required to burn 50 grams of carbon?

The equation for this action is C+O<sub>2</sub>→CO<sub>2</sub>. This shows that 12 parts by weight of carbon combine with 32 parts by weight of oxygen to form 44

parts of carbon dioxide. If 12 gms. of carbon react with 32 gms. of oxygen, 1 gm. of carbon will react with  $32 \div 12$ , or 2.66 gms. of oxygen, and 50 gms. with  $50 \times 2.66$  gms., or 133.3 gms. of oxygen. Or, the problem may be expressed in the form of a proportion:

$$X = \frac{32 \times 50}{12} = 133.3 \text{ gms.}$$

In solving a problem, the formula weights of the two substances involved in the solution should be set down under the formulas of the compounds. Thus, if it is required to find how many grams of  $\rm H_2O_2$  can be obtained from 40 grams of  $\rm BaO_2$ 

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$
  
169.37 34.016

Then

169.37: 34.016:: 40: X

Or

$$\frac{\frac{169.37}{34.016}}{\frac{40}{X}} = \frac{40}{X}$$

$$X = \frac{34.016 \times 40}{169.37} = 8.03 \text{ gms. H}_2\text{O}_2$$

#### **EXERCISES**

- 1. Define atom, molecule, symbol, formula, equation, formula weight, gram-molecular weight.
- State the four fundamental laws of chemical action treating of material changes.
  - 3. Give a full statement of the atomic theory.
- 4. Give names of four types of chemical reactions. Define each. Give two equations to illustrate each.
  - 5. Solve problems 2, 3, 4, 5, 7, 8, 9, 13, and 14, pages 102-103.

## SEND EXERCISES FOR LESSONS I=V TO THE SCHOOL

## LESSON VI

## CARBON AND CARBON DIOXIDE

## Assignment: Chapter X, McPherson and Henderson

Occurrence of carbon. Carbon is a familiar element, occurring in impure form in coal and charcoal. Its compounds are widely distributed and are commonly met with in our daily life. Carbon, together with hydrogen, is a necessary constituent of all of that large class of compounds known as organic. By organic compounds was originally meant those associated with living mat-

ter, plant or animal. That meaning is no longer satisfactory as many organic compounds have been made without association with living things.

Yet the composition of all living matter very largely consists of these so-called organic compounds, or compounds of carbon and hydrogen and their derivatives. Such compounds are also found in natural gas, petroleum, and the distillation products of wood and soft coal. Limestone and marble are carbonates and are salts of an acid of carbon, just as the chlorides are salts of an acid of chlorine.

Forms of carbon. The element carbon is capable of existing in three allotropic forms. Two of these are crystalline and one amorphous. The crystalline forms are diamond and graphite. The amorphous form is pure charcoal made from sugar. A complete statement of the properties and preparation of diamond and graphite will be found on pages 117 and 118.

That these substances are allotropic, that is to say, that they consist of the same kind of matter but differ as to the amount of energy contained, is shown by experiments in the combustion of them. If 1 gm. of each be burned, the same weight of carbon dioxide will be obtained but different amounts of heat energy will be set free from the several forms.

Natural varieties of amorphous carbon. Several varieties of amorphous carbon are well known; the differences in properties are due to impurities or to variation in physical structure resulting from the methods of formation or manufacture. Some occur in nature as the various forms of coal. Anthracite, or hard, coal is chiefly elementary carbon. Soft, or bituminous, coal contains a considerable part of the carbon combined with other elements, chiefly hydrogen. Oxygen, nitrogen, and sulfur are found also.

Coal deposits are considered to be the result of a process of destructive distillation occurring in nature. In a very early geological age of the earth's history the atmosphere contained a much larger percentage of carbon dioxide than it does at present. Carbon dioxide is a necessary plant food. In that age there is evidence that a very rank and luxurious form of vegetation existed. In the course of successive changes in the earth's surface this heavy vegetation became covered over with earthy deposits.

Thus confined, the heat of the earth carried on a decomposition which resulted in the formation of deposits of coal containing varying amounts of elementary carbon.

The older formations are anthracite, the later formations bituminous coal. Natural gas is a product of this process of natural distillation. Lignite, a substance closely related to bituminous coal, is a still younger formation and contains only a small amount of carbon as the element. Peat is another form of vegetable matter in the early stages of decomposition. It is largely mixed with earthy matter but, when dried, makes a satisfactory fuel.

Artificial varieties of amorphous carbon. Other forms of amorphous carbon can be manufactured from carbon compounds. Coke is made by the destructive distillation of bituminous coal, that is, by the heating of the coal in a retort or furnace from which air is excluded, so that combustion does not take place. The coke consists of carbon and the mineral matter of the coal. Other products of the heating of bituminous coal in the absence of air are coal gas, ammonia, and coal tar. All are valuable and will be considered fully in later lessons.

Wood charcoal is prepared from wood in a way similar to that for making coke from coal. Among the other products of the destructive distillation of wood are wood alcohol and acetic acid. Lampblack is a product of the destructive distillation of oils and gas containing high percentages of carbon. Bone black, or animal charcoal, is the product of the destructive distillation of bones and refuse animal matter.

Varieties of amorphous carbon not allotropic. These several forms of carbon are simply varieties of amorphous carbon and not allotropic modifications of the element. An experiment in combustion will show this to be the case.

Since these forms are impure, such amounts must be taken for combustion as will contain the same amount of carbon. This can be done by taking such amounts of the substances as will give on combustion equal weights of carbon dioxide. If the different forms were allotropic, each would generate on combustion a different amount of heat energy. In this experiment, however, it would be found that for equal weights of carbon dioxide formed equal

amounts of heat energy would be liberated. Therefore, they are not allotropic, since their carbon contains the same energy.

Properties and uses. Many of the physical properties of carbon vary with the different allotropic forms. All, however, are odorless, tasteless, insoluble in water, and volatile only in the intense heat of the electric arc. Bone black, especially, has the property of absorbing colors and odors, and liquids are purified and decolorized by being passed through bone-black filters.

Carbon is used in gas masks because of this property of absorbing gases. During the War it was so used. A special form of carbon for this purpose was prepared from coconut shells, peach and prune seeds, etc. Cane-sugar solutions are decolorized prior to the crystallization of the granulated sugar by being filtered through carbon.

In its chemical behavior carbon is characterized by its inactivity. It does not act on the ordinary acids except those that are strong oxidizing agents. At high temperatures it will combine with oxygen, sulfur, and hydrogen. With some metals it forms carbides.

Its chief use is as a fuel. However, large amounts are used as a reducing agent because of its great tendency to combine with oxygen. In obtaining metals from their oxides carbon serves as the reducing agent; in the blast furnace carbon reduces the iron oxide to iron; other examples are the reduction of zinc and tin oxides with carbon.

Carbon dioxide. There are two well-known oxides of carbon: carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO). Only the former will be studied at this time. Carbon dioxide occurs in the atmosphere, about 3 parts in 10,000. It is a colorless gas formed by the combustion in oxygen of substances containing carbon, such as the ordinary fuels; it is also a product of respiration, being formed by the oxidation of foods in the body; and fermentation and decay of organic matter likewise form it. Its presence in the atmosphere is essential to plant life.

For many purposes it is prepared by the action of an acid on a carbonate. Calcium carbonate (CaCO<sub>3</sub>) is usually used because of its common occurrence. The following equation represents the action when hydrochloric acid is used:

CaCO<sub>3</sub>+2HCl→CaCl<sub>2</sub>+H<sub>2</sub>O+CO<sub>2</sub>

For a description of the method see page 123. It may also be prepared by heating limestone as in the preparation of lime (CaO). It has been prepared commercially by fermentation in connection with the manufacture of malt beverages.

Properties and uses. Carbon dioxide is a very heavy gas and can be poured like water. For this reason it sometimes collects in wells and mines. It is 1.5 times as heavy as air. It is colorless and odorless. It can be liquefied and solidified; the solid is obtained by the cooling effect produced by the sudden expansion of the substance when released from pressure (page 125). Solid carbon dioxide has a low enough temperature to freeze mercury; it is used in surgery for freezing local areas in minor operations.

Carbon dioxide cannot be burned, as it contains all the oxygen that carbon is capable of holding in combination. Neither will it support combustion as it is a very stable compound. The word "stable" is used in the sense of not being easily separated into its elements. It holds its oxygen in firm combination and cannot give up any to support the combustion of other substances.

Its presence in the atmosphere can be shown by its action with calcium hydroxide, or limewater, (Ca(OH)<sub>2</sub>), a white precipitate being formed when the gas is passed into limewater. The chemical change is represented as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Carbon dioxide is a plant food and is absorbed from the air by the leaves.

It is the gas that causes effervescence in many beverages, such as soda water, mineral waters, champagne, and beer; the gas is held in solution under pressure and escapes when the cork is removed. Its use as a fire extinguisher is important. In all portable fire extinguishers, or chemical fire engines, as they are sometimes called, a bottle of concentrated sulfuric acid is upset or broken into a solution of sodium carbonate. The gas formed creates pressure to force the saturated solution of carbon dioxide out of the generator (see page 126).

Carbon dioxide is not a poison, though persons could not live in an atmosphere of it since it would exclude oxygen from the lungs and death would result from lack of oxygen, as it does in cases of strangulation. Other compounds of carbon will be studied in Lessons XVII and XVIII.

#### **EXERCISES\***

- 1. State the occurrence of carbon in nature.
- 2. Name the allotropic forms and varieties of carbon.
- 3. Give an experiment which will show that diamond and graphite are allotropic.
  - 4. Give one to show that anthracite coal and coke are not allotropic.
  - 5. How may diamonds be made artificially?
  - 6. Give the sources and properties of diamonds.
  - 7. Give the sources and preparation of graphite.
  - 8. Give the properties and uses of graphite.
  - 9. How is pure charcoal made?
  - 10. Discuss the sources, origin, and properties of various kinds of coal.
- 11. Give methods for making coke, charcoal, bone black, and lamp-black.
  - 12. State the physical properties and chemical conduct of carbon.
  - 13. Give the uses of carbon.
  - 14. Where is carbon dioxide found, and how is it formed by nature?
- 15. Give the methods for preparing carbon dioxide and the equations where possible.
  - 16. How is solid carbon dioxide made? What are its uses?
  - 17. Give the properties and the chemical conduct of carbon dioxide.
- 18. What are the uses of carbon dioxide? How is it used as a fire extinguisher?
  - 19. Solve problems 7, 12, 15, and 16, page 127.
  - 20. Answer questions 4, 5, 9, 11, 13, and 14, page 127.

## LESSON VII

## NITROGEN; THE ATMOSPHERE

### **NITROGEN**

Assignment: Chapter XI, McPherson and Henderson

Occurrence of nitrogen. This element is very plentiful, but not so widely distributed as some others. It occurs chiefly in the atmosphere, of which it constitutes 78 per cent by volume, this source seeming to be inexhaustible.

Air was at one time thought to be a simple substance. Rutherford obtained nitrogen from air by burning charcoal and

<sup>\*</sup>Prepare this set of Exercises and hold it until those for Lessons VII, VIII, IX and X are also prepared and then send all five sets to the School.

phosphorus in it. Lavoisier called the residue (nitrogen) azote, meaning unable to support life; the name "nitrogen" is used because this element is a characteristic constituent of niter, or saltpeter. The chemical name for saltpeter is potassium nitrate (KNO<sub>3</sub>). Nitrogen also occurs in sodium nitrate (NaNO<sub>3</sub>), found in Chili and called *Chili saltpeter*. Many organic compounds contain nitrogen, for example, those that compose the substances known as proteins. Proteins are an important class of foods as they are the tissue builders. The human body contains 3 per cent nitrogen.

Preparation. For commercial purposes nitrogen is prepared, along with oxygen, by the liquefaction of air. The nitrogen, having a lower boiling point, boils off first and can be collected. Liquid air will be considered later in this lesson. Nitrogen prepared in this way contains some oxygen but serves for those industrial purposes in which nitrogen is one of the raw materials. Nitrogen is obtained from the air by other methods based upon the action of some substance which will combine with the oxygen and leave the nitrogen. Phosphorus and copper are used (see page 129).

None of these methods gives pure nitrogen. There are several rare elements in the air which are left along with the nitrogen when the oxygen is removed. As they are more inert chemcally than nitrogen, they do not interfere with its use for many purposes. Pure nitrogen can be prepared only from compounds which contain it. Ammonium nitrite is most often used. This compound is so unstable that it cannot be obtained in the market, but has to be prepared fresh at the time of its use; its decomposition as fast as it is formed produces the nitrogen. The two steps are shown by the following equations:

# $NaNO_2+NH_4Cl \rightarrow NaCl+NH_4NO_2$ $NH_4NO_2 \rightarrow 2H_2O+N_2$

Properties. In its chemical behavior nitrogen is less active than all the elements previously studied and much less active than oxygen and hydrogen. It shows no tendency to combine with other elements at ordinary temperatures. It combines with magnesium, oxygen, hydrogen, and a few other elements with diffi-

culty and only at high temperatures. Conditions can be established under which nitrogen and hydrogen will combine to form ammonia on a commercial scale. The same is true for the reaction between oxygen and nitrogen. When ammonia and nitric acid are studied in Lesson XII, these reactions will be taken up again.

The compounds of nitrogen with metals are called nitrides. Its compound with hydrogen is ammonia (NH<sub>3</sub>), a common and useful substance. With oxygen it forms a number of oxides. These compounds will be studied later. Like carbon dioxide it is not a poison, but people could not live in an atmosphere of pure nitrogen because of the lack of oxygen. Its physical properties are stated on page 131.

Uses. Nitrogen is used to fill thermometers and light bulbs and to prepare ammonia, nitric acid, and calcium cyanamide, which substances are used in making fertilizers (see page 462). Nitrogen is necessary to plant life as it is the element that builds up the protein tissues; but plants have no mechanism for absorbing free nitrogen, they can only absorb it when it exists in the form of water-soluble compounds which can be taken up from the soil by their roots. Nitrogen, to be available, must be converted into ammonium salts, nitrates, or compounds which on action with water will form one of these. Many efforts have been made to devise methods for fixing atmospheric nitrogen so that the supply of nitrogen fertilizer material might be increased.

In this connection the action of such plants as clover, alfalfa, beans and peas, belonging to the family of legumes, is interesting. Indirectly they assimilate nitrogen. They have tubercles, or nodules, on their roots in which a form of bacterial life develops. These microörganisms are able to bring about the union of nitrogen and oxygen, forming compounds which form water-soluble nitrates with substances in the soil. Some of these nitrates are absorbed by the plant itself; others remain in the soil to increase its fertility (page 132).

Rare elements. Argon, helium, neon, krypton, and xenon are rare elements occurring in the air in small amounts. They are similar in properties and noted for complete chemical non-activity. They form no known compounds. Argon is the most plentiful and helium the most important. Next to hydrogen,

helium is the lightest element. During the late war considerable quantities of helium were discovered in the gas from certain oil wells in Texas. The quantity was great enough to make it possible to use it to fill war balloons. It has the advantage over hydrogen of being non-combustible, which means that when the gas bag is punctured by an enemy shot, there is no combustion of the balloon but a slow leakage which enables the observer to come to the earth in safety.

#### THE ATMOSPHERE

## Assignment: Chapter XII, McPherson and Henderson

Composition. Air was formerly considered an element, but the obtaining of oxygen and nitrogen from it contradicts this idea. Besides these elements it contains water vapor and carbon dioxide in small amounts as well as the rare elements. Consult page 135 for the percentage of each constituent. Water vapor varies but the amounts of the others are essentially constant (page 136).

Of these constituents oxygen is necessary to support the life of animals, carbon dioxide to support the life of plants, and water vapor to support the life of both, as it prevents evaporation of water from the tissues. Nitrogen is essential to dilute the others, especially oxygen, and so to diminish the intensity of its action.

Quantitative analysis of air. The quantitative analysis of air consists in determining the amounts of each of the four principal constituents, using the reactions described on pages 136–137. In actual practice it is necessary to start with a measured volume of air and apply these reactions in a certain sequence. For example, air is passed through a gas meter to measure its volume, and then through a weighed vessel containing calcium chloride (CaCl<sub>2</sub>), which is a good drying agent. The increase in the weight of the vessel is the weight of the water in the measured volume of air. The remaining air is then passed through a weighed vessel containing sodium hydroxide or calcium hydroxide, which absorbs the carbon dioxide:

## 2NaOH+CO<sub>2</sub>→Na<sub>2</sub>CO<sub>3</sub>+H<sub>2</sub>O

The air is next passed over, or allowed to stand for a time in contact with, yellow phosphorus, which combines with oxygen. The

loss in volume measures the amount of oxygen. Finally the gas left may be passed over hot magnesium, when the nitrogen combines with it to form magnesium nitride (Mg<sub>3</sub>N<sub>2</sub>), leaving only the rare elements of the air.

Changes in composition. The average composition of the air remains nearly constant, but there are continual changes tending to increase or decrease oxygen, carbon dioxide and water vapor. Carbon dioxide is added by the exhaled breath of animals, the burning of carbon compounds (fuels), the decay of organic matter, and escapes from volcanoes. Carbon dioxide is removed by the action of plants, which absorb it through their leaves. Sunlight enables plants to utilize the carbon to build up the carbon compounds of their tissues. The weathering of rocks also absorbs carbon dioxide.

Oxygen is added to the air by the action of plants. It is removed by the inhalation of animals in breathing and by the combustion of fuels. These changes, which offset each other, together with the mixing influence of the winds, keeps the composition of air constant.

Air a mixture. Two reasons for considering air to be a mixture are given on page 139: (1) The composition of air dissolved in water is not the same as that of undissolved air. (2) Air does not have a constant boiling point as a compound always has. A third reason may be given. The formation of a compound always is evidenced by some energy change. Nitrogen and oxygen when brought together, in the proportions for forming air, give a product which is not different from air, but there is no evidence of an energy change, such as evolution or absorption of heat.

Impure air. In rooms and halls where people live or meet, a frequent renewal of the air is necessary to health. The bad effects of stale air arise from substances exhaled from the lungs. It is not supposed that the ill effects are due to an excess of carbon dioxide or to a lack of oxygen in ordinary cases; they are due, rather, to an excess of moisture, high temperature, and the presence of certain poisonous organic substances exhaled with the carbon dioxide. The air should be in constant slow motion, otherwise that near a person's body becomes saturated with moisture (page 140).

Liquid air. The properties of liquid air are stated on page 141. It is used in preparing oxygen and nitrogen for industrial purposes. The method of liquefaction is discussed on page 108. Dewar flasks are used for holding liquid air. They have a double wall with a vacuum between. The common thermos bottle is constructed on the same plan.

Artificial ice. The principle used in making liquid air is that of compression and sudden expansion. The suddenly expanding gas absorbs great quantities of heat and is used to cool other portions of the substance below the liquefaction point. The same principle is applied in making artificial ice. Ammonia is compressed and allowed to expand through a small valve into pipes running into brine, or salt solution, which will not freeze until quite a low temperature is reached; as a result of the rapid expansion of the ammonia the brine becomes so cold that distilled water in tanks placed in it is cooled to the freezing point (page 111).

#### **EXERCISES**

- 1. Give the sources of nitrogen.
- 2. How is nitrogen obtained for industrial purposes?
- 3. Describe the method for liquefying air.
- 4. How are phosphorus and copper used to obtain nitrogen?
- 5. Write equations and explain the method for making pure nitrogen.
- 6. Give the physical properties of nitrogen.
- 7. Discuss the chemical conduct of nitrogen.
- 8. What are the uses of nitrogen?
- 9. Explain the action of legumes on nitrogen.
- 10. Name the rare elements. What is the use for helium?
- 11. Give the composition of the air.
- 12. How could this composition be determined quantitatively?
- 13. Discuss changes in the composition of the air.
- 14. Why is air believed to be a mixture?
- 15. State the properties of liquid air.
- 16. What is a Dewar flask; a thermos bottle?
- 17. Describe the manufacture of artificial ice.
- 18. Solve problems 9, 10, 11, 12, and 13, page 134.
- 19. Solve problems 7, 8, 9, 10, and 11, page 142.
- 20. Answer questions 1, 3, 4, and 5, page 134.
- 21. Answer questions 2, 3, 4, 5, and 6, page 142.

### LESSON VIII

## **SOLUTIONS: IONIZATION**

# Assignment: Chapter XIII, McPherson and Henderson

Definition. Most of us are familiar with the term solution, and there is a widespread tendency to think of it as referring to something liquid. Most solutions are of this kind, but some very common ones are solids, as glass and brass. However, take a common example, water and sugar; one substance is a liquid, the other a solid; on adding the sugar to the water, the solid crystals disappear and the particles of sugar can no longer be distinguished, even by the aid of a very high-power microscope.

On the other hand, that change fails to show the characteristics of an ordinary chemical change. Something has taken place that represents a condition between that of mixture and compound. Some weak kind of chemical action may have occurred, but it seems best at this elementary stage of the study of chemistry to consider solutions as a result of physical changes.

A property to be especially noted is that solutions are homogeneous to the smallest part, and that mechanical methods will not separate the substances. Another property of solutions is the variation in composition. Salt and water dissolve in all proportions up to a certain maximum. Alcohol and water mix in all proportions without limit either way. A solution containing 5 per cent salt and one containing 10 per cent salt are not sufficiently different to be called different substances.

A solution is defined as a homogeneous mixture of two or more substances which cannot be separated by mechanical means and whose composition may vary. The substance which is thought of as going into solution is the solute. The one that does the dissolving is called the solvent.

Solution of gases in liquids. Each state of matter is found dissolving in every other state of matter. Most solutions are those where a liquid is the solvent. Gases dissolve in liquids—some, like oxygen and hydrogen, to a slight extent only; others, like ammonia and hydrogen chloride, to a large amount; and still others, like carbon dioxide, dissolve more moderately (consult the

table on page 144). The nature of the gas, therefore, determines the amount of solubility; so does the nature of the solvent; for example, water and alcohol do not dissolve the same amounts of a gas.

Increase of pressure increases the amount of solubility, the increase being proportional to the pressure. This is the law of Henry (page 145). Under high pressure large quantities of gas may be held in solution. The excess gas in solution suddenly escapes when the pressure is removed, causing effervescence. An example is common soda water, or other effervescing drinks, which are bottled with the gas dissolved under pressure. Generally an increase of temperature decreases the amount of the gas which will remain in solution.

Solids in liquids. Nature of the solid, nature of the solvent, and temperature are the factors that influence the amount of solid which dissolves. Different substances vary widely in the amount which will be dissolved. No solid is entirely insoluble in water, but barium sulfate is almost so. Usually, increasing the temperature of the solvent will cause it to dissolve more of the solid (consult the table on page 147). Calcium sulfate is seen to be an exception.

Molar solutions. Concentration of solutions may be expressed by parts per hundred or grams in 100 cc. It is usually more satisfactory to use a method which shows the formula weight of the substance in a certain volume of solution (not of solvent). This is called a *molar solution*. A molar solution is obtained by dissolving the formula weight, or molecular weight, in grams of the substance in enough solvent to make 1 liter of solution.

The student must clearly understand that equal volumes of all molar solutions contain the same number of molecules. Take two substances, one having twice the molecular weight of the other. We do not know how many molecules there are in a gram; but, if we take 2 gms. of one and 1 gm. of the other, we have taken the same number of molecules. An example may make this plainer. Assume two piles of shot, one kind weighing 2 gms. each, the other weighing 1 gm. Assume that you do not know the number of grams in a pound, as above you do not know the number of molecules in a gram. If, now, you weigh out 2 lb. of the 2-gm. shot

and 1 pound of the 1-gm. shot, you do not know how many shot you have weighed in either case, but it is clear that the number is the same in both cases. In like manner, molar, or gram-molecular, solutions contain the same number of molecules in equal volumes.

Saturation. Some liquids dissolve in each other in all proportions, but with solids (and some liquids too), a point is reached where the solvent will dissolve no more. This is a saturated solution. When some of the solid remains in contact with the solution without change in concentration, the solution is said to be saturated. If the solvent evaporates from a solution, the solid separates out, usually in crystalline form. If a nearly saturated solution is made at high temperature, the solid in excess of the quantity required to saturate the solution at ordinary temperature usually separates out on cooling.

In a few cases a condition of supersaturation exists. Sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), commonly called "hypo," gives a good illustration of this. Several grams will dissolve in a few drops of water, if heated. The solution may be cooled without crystals separating as long as it is undisturbed. Dust particles or a small crystal of the "hypo" will cause immediate crystallization. A supersaturated solution is one which contains more of the solute in solution than the solvent will dissolve at the given temperature. The excess of solute, which went into solution at a higher temperature, does not separate out on cooling until disturbed in some way.

Properties of solution. 1. Tendency to uniformity. A solution tends to become uniform, the heavy solid rising opposite to the force of gravity. This is a similar tendency to diffusion of gases. The process is slow unless aided by stirring. Once the solution becomes uniform, the uniformity is permanent.

- 2. Effect on boiling and freezing points. A solid dissolved in a liquid raises the boiling point and lowers the freezing point of the solvent. This change in boiling point or freezing point of the solvent is proportional to the molecular concentration. (Reread paragraph on molar solutions.) Thus, it appears that these changes are caused by the number and not by the kind of molecules.
- 3. Electrolysis. Some solutions conduct the electric current and some do not. Salt dissolved in water is a conductor; sugar

dissolved in water is not. A solution which conducts the current is called an *electrolyte*. This conductivity is always accompanied by a decomposition of the substance in solution. This decomposition is called *electrolysis*. The electrodes are the terminals of the wires by which the current enters and leaves the solution. The positive electrode is called the *anode*, the negative one is called the *cathode*.

Freezing points of conductors. A study of solutions shows that such substances as sugar, glucose, alcohol, and other organic compounds, if soluble in water, form solutions which do not conduct the current, while sodium chloride, copper sulfate, sulfuric acid, and other inorganic compounds of the classes of acids, bases, and salts do form conducting solutions. It is further noticed that those substances whose solutions conduct the current affect the freezing and boiling points of the solvent abnormally.

This will be made clear by a comparison of the behavior of solutions in water of sugar, glucose, and salt. Take molar solutions of each, that is, the molecular weight in grams dissolved in 1 liter of solution. Such solutions of sugar and glucose will freeze at 1.86° below 0° C. All molar solutions which do not conduct the electric current give this same lowering of the freezing point. A molar solution of common salt, however, freezes at a still lower temperature, about 2.79° below zero. Other salts and acids and bases give a similar abnormally large lowering of the freezing point. If the salt solution is diluted, the actual lowering is less, but the actual lowering multiplied by the amount of dilution gives a molecular lowering which becomes greater with the greater dilution and which approaches a maximum value of two times 1.86°. Other compounds, like sulfuric acid, approach a maximum lowering of three times 1.86°.

The theory of ionization. Because organic compounds uniformly lower the freezing point to 1.86° below zero, it was accepted that the lowering was caused by the number of molecules present in the solution, equal volumes of all molar solutions containing equal numbers of molecules. However, compounds giving a still lower freezing point are numerous and include such important compounds as the acids, bases, and salts, as shown above for common salt and sulfuric acid.

Arrhenius proposed to explain these exceptions by assuming that such substances in solution have some of their molecules dissociating into parts, thus forming a greater number of particles to produce a greater lowering of the freezing point. Sodium chloride molecules break up into two particles. The percentage of dissociation increases with increased dilution and when all the molecules are dissociated, we have twice as many particles in the solution as original molecules. Therefore, the maximum lowering of the freezing point is twice the normal lowering, or twice 1.86°. Since sulfuric acid gives a maximum lowering of three times 1.86°, each molecule dissociates into three particles in very dilute solutions.

Explanation of conductivity. Until this theory of dissociation of molecules in solution was proposed, there was no satisfactory explanation of conduction of the electric current by solutions. This conduction becomes clear if we assume that the parts into which the molecules dissociate are electrically charged, some positively and some negatively. If the current is passed through a solution of copper chloride, metallic copper is deposited at the negative pole and chlorine at the positive pole. It is believed that, in the formation of the solution, some of the copper chloride molecules dissociate into parts, which at the same time become electrically charged.

These charged parts of the molecule are called *ions*. The copper ions have positive charges, and the chlorine ions negative charges. These are in motion in every direction before the current is passed. When the current is passed, the positive ions are attracted to the negative pole, while the negative ones go to the positive pole. Upon arriving at the poles, the ions become discharged, giving up their charges to the poles. In this way they carry the current through the solution.

It is to be noted that those solutions which have an abnormally great lowering of the freezing point are the same ones which are conductors. The same theory explains both sets of facts.

Statement of the ionic theory. 1. Some molecules of some substances when they go into solution dissociate into parts called ions.

- 2. These ions are electrically charged. For that reason their properties differ from those of the atom or molecule.
- 3. The positive charges always equal the negative charges. Some ions carry two or more charges, so the number of positive and negative ions is not always equal. Copper chloride (CuCl<sub>2</sub>) dissociates into Cu, carrying two positive charges, and into two chlorine ions, each carrying a single negative charge. Positive ions are called *cations*. Negative ions are called *anions*.
- 4. All compounds do not ionize. Those that do ionize do so in varying degrees. Hydrogen chloride is ionized by water to a large degree, while acetic acid is but slightly ionized, and sugar not at all.
- 5. Not all solvents produce ionization. Benzene will not ionize hydrogen chloride. The same compound is ionized to different amounts in different solvents. Water is the best ionizing solvent; alcohol also produces ionization, but to a much less extent than water. Dilution of the solution increases the percentage of ionization.

Electrolysis. The theory of ionization explains the electrolytic decomposition of substances in solution. This method is used in copper, nickel, and silver plating and in electrotyping. A few examples will be given.

With a solution of copper chloride, the copper ions carrying two positive charges travel to the cathode when the current is turned on. They give up their charge to this pole and deposit on it as molecules of copper, since copper has no action on the water present. To the anode pole chlorine comes and loses its charge. The chlorine escapes as a gas. It has only a slight action with the water, if the solution is concentrated.

Sulfuric acid was used in the so-called electrolysis of water. In reality it was the sulfuric acid that was decomposed by the current and not the water. That the elements of water were liberated was due to a secondary action at the anode. In solution sulfuric acid forms two positive hydrogen ions and one sulfate ion (SO<sub>4</sub>) carrying two negative charges. When the current is passed, two hydrogen ions go to the cathode, are discharged, and are liberated as a molecule of hydrogen. For each molecule of hydrogen, a single sulfate ion is discharged at the anode. Here it

acts with water to form sulfuric acid, and one atom of oxygen, which of course forms molecules, escapes as a gas.

Sodium hydroxide is a base. Its molecule ionizes to form Na+ and OH- ions. At the cathode the sodium is discharged when a current of electricity is turned on. Unlike the copper it does not deposit, neither does it escape like hydrogen. Sodium is a very active metal chemically and reacts with the water of the solution to form hydrogen, according to the following equation:

At the anode the OH ions become discharged but do not escape as such. They combine to form water and oxygen:

$$4OH\rightarrow 2H_2O+O_2$$

Properties of electrolytes. The properties of an electrolyte will depend upon both the ions and the molecules present. Ions are very much more active than molecules, so they usually are responsible for the chemical properties of the solution.

Silver nitrate solution will precipitate silver chloride from aqueous solutions of all chlorides because chlorides form the chlorine ion. It will not precipitate silver chloride from a water solution of potassium chlorate; potassium chlorate contains chlorine, but, instead of forming the chlorine ion, it forms the ions K<sup>+</sup> and ClO<sub>3</sub>-. Neither will silver nitrate precipitate the chlorine from organic chlorides which do not ionize. Some ions have a characteristic color, as Cu<sup>++</sup> is blue, Fe<sup>+++</sup> yellow, and Cr<sup>+++</sup> green.

#### **EXERCISES**

- 1. Define the following terms: solution, solute, solvent, saturated solution, supersaturated solution, molar solution, electrolysis, electrolyte, cathode, anode, ion, cation, anion.
- 2. Discuss factors affecting the solubility of a solid and of a gas in liquids.
- 3. State the effect of a dissolved solid upon the boiling and freezing points of solutions.
- 4. Explain why molar solutions contain equal numbers of molecules in equal volumes.
  - 5. What classes of compounds form solutions which are conductors?
  - 6. State the points in the theory of ionization.
  - 7. Give some reasons in support of the ionic theory.
  - 8. How do sugar and salt affect the freezing point of their solutions?

- 9. Explain the electrolysis of copper chloride ( $CuCl_2$ ); of sodium hydroxide (NaOH).
  - 10. Solve problems 8, 9, 10, and 11 on page 158.
  - 11. Answer questions 2, 3, 4, 5, 6, and 7 on pages 157 and 158.
  - 12. Answer questions 12, 13, and 14 on page 158.
  - 13. Why is salt brine used in making artificial ice?

### LESSON IX

## CHLORINE; SODIUM

#### CHLORINE

# Assignment: Chapter XIV, McPherson and Henderson

Occurrence. Chlorine is a very active non-metallic element. Because of its great activity it is found in nature only in the combined state, never as the free element. In this respect it is unlike the elements already studied. Sodium chloride is the most abundant compound of chlorine, and it is from this substance that chlorine is made.

Preparation. For commercial purposes chlorine is prepared by the electrolysis of a concentrated solution of sodium chloride. Chlorine escapes at the anode and sodium hydroxide (NaOH) is formed at the cathode by the action of sodium with water (pages 155 and 161). Sodium chloride is cheap, and sodium hydroxide has many uses (see pages 175 and 176). The chlorine obtained is either compressed in metallic cylinders or absorbed in bleaching powder (page 427), from which it can easily be obtained.

For preparing chlorine in small quantities, as in a laboratory, two other methods are used. Both involve the setting free of chlorine from hydrochloric acid. The substances used to do this are manganese dioxide and potassium permanganate. The reactions may be explained as oxidizing actions, the manganese dioxide (MnO<sub>2</sub>) and potassium permanganate (KMnO<sub>4</sub>) furnishing the oxygen to combine with the hydrogen of the acid to form water and set free the chlorine.

In the case of manganese dioxide another explanation is possible, as is shown by the equations on page 159. It is frequently the practice to make the hydrochloric acid at the time when, and in the apparatus where, the chlorine is to be prepared. Sodium chloride, sulfuric acid, and manganese dioxide are added. The following equation represents the final result of the reaction:

 $MnO_2+2NaCl+2H_2SO_4\rightarrow Na_2SO_4+MnSO_4+2H_2O+Cl_2$ 

Sometimes free oxygen is used to set chlorine free from hydrochloric acid, but the yield is small.

Properties. Chlorine is a gas, yellowish-green in color. It can be easily liquefied, is 2.5 times as heavy as air, soluble in water, has a suffocating odor, and is very irritating upon the nose, throat, and lungs (page 162).

Chemical conduct. Chlorine is a very active element with negative, or non-metallic, properties. Like oxygen it combines with most of the other elements but it is much more active than oxygen at ordinary temperatures. Many of the elements, like phosphorus, arsenic, antimony, iron, and sodium, burn in it to form chlorides. Even gold and platinum are tarnished by it.

It will vigorously support the combustion of hydrogen, giving a greenish-yellow flame and forming hydrogen chloride (HCl). Light will cause a mixture of hydrogen and chlorine in equal volumes to explode. Chlorine has such a strong tendency to combine with hydrogen that it will extract it from compounds containing it. Sulfur and hydrochloric acid are formed when chlorine is passed into a solution of hydrogen sulfide

## Cl<sub>2</sub>+H<sub>2</sub>S→2HCl+S

Turpentine decomposes with the formation of soot when a piece of paper, moist with it, is introduced into a jar of chlorine, hydrochloric acid (HCl) and carbon being formed. Chlorine will set oxygen free from water. Sunlight increases this action (page 164). Chlorine solution in water is, therefore, a good oxidizing agent.

Chlorine is a strong bleaching agent, but water is necessary to the action as experiment shows that dry chlorine will not bleach pieces of colored calico which are quickly bleached if wet (page 165). It would seem, therefore, that it is the oxygen set free from the water that is the immediate agent in bleaching the cloth. Only those colored substances can be bleached whose coloring matter can be oxidized to colorless compounds. Printer's ink, which is made of carbon, cannot be bleached (page 165).

Uses. Besides being used largely as a bleaching agent, chlorine is used as a germicide or disinfectant in the form of either the free element or compounds from which it is readily set free, like bleaching powder. Cotton cloth is now bleached by the use of chlorine. It is used to kill microörganisms in drinking water, as in city water supplies, and to purify water for the army. Chlorine was the first of the cloud gases used in the Great War, and later many of the gas bombs contained it or some of its compounds.

Nascent state. The oxygen set free by the action of chlorine on water is much more active than ordinary oxygen. It bleaches colored cloth which would not be bleached by pure oxygen or by air. The difference is due to the fact that the bleaching is done just at the time when the oxygen is set free from combination with water and before it has combined with itself to form molecules of oxygen. It is at this time in the atomic state, and none of its energy is used up in holding its atoms in a molecule. In this atomic state it is much more active. This state is called the nascent state. It is the state existing at the time of its liberation from compounds. The root of the word "nascent" means to be born.

### HYDROGEN CHLORIDE

Preparation. The compound of hydrogen and chlorine may be made by the direct union of chlorine and hydrogen as has been shown. Hydrogen chloride can be more conveniently made by another method. Common salt (NaCl) is treated with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and hydrogen chloride are formed:

For commercial purposes it can be prepared by using the same reaction (page 167). It is also prepared commercially from sodium chloride (NaCl) and sodium hydrogen sulfate (NaHSO<sub>4</sub>) (page 168):

The hydrogen chloride escapes as a gas and is dissolved in water. This solution is the hydrochloric acid of commerce. When pure it is colorless; but frequently it is colored yellow by impurities. The impure acid is called muriatic acid, meaning the acid of sea salt.

**Properties.** Its solubility in water, irritating odor, and gaseous state are its important physical properties. One volume of water dissolves 506 volumes of hydrogen chloride gas. Other physical properties will be found stated on page 169.

Composition. By the electrolysis of a solution of hydrogen chloride, or by combining the two gases, it can be shown that 1 volume of hydrogen and 1 volume of chlorine combine to form 2 volumes of hydrogen chloride. Like the volume composition of water this fact must be remembered for future use in selecting the standard of molecular weights. By weight, hydrogen chloride contains 35.18 parts of chlorine and 1 part of hydrogen to every 36.18 parts of the gas.

Hydrochloric acid. Hydrogen chloride as a gas is little used and is inactive. Its solution in water, hydrochloric acid, is very active because of the formation of hydrogen and chlorine ions. It is one of the common acids (page 169). As such it has a sour taste, turns litmus red, and is acted upon by certain metals with the replacement of its hydrogen by the metal. Iron, zinc, and sodium so act. The equations for these actions are found on page 171. It acts with bases, like sodium hydroxide (NaOH), to form water and a salt:

## HCl+NaOH→H<sub>2</sub>O+NaCl

Hydrochloric acid under certain conditions is a reducing agent—not so active a reducing agent as some other compounds, but it will give up its hydrogen to compounds like nitric acid and potassium permanganate. The equations for these actions will be taken up when these compounds are studied. Hydrochloric acid is a very strong acid. What is meant by the strength of an acid will be learned in the next lesson.

#### SODIUM

## Assignment: Chapter XV, McPherson and Henderson

Metals. Elements are divided into two great classes, metals and non-metals. Chemically the two classes have opposite properties, and they have wide differences in physical properties. The

metals are solids, except mercury which is a liquid, they have a metallic luster, and they conduct heat and electricity. The chemist sometimes distinguishes between the chemical properties of the metals and the non-metals by describing the metals as positive and the non-metals as negative. A metal is an element which may become a positive ion upon solutions being made of its compounds. In this sense hydrogen is a metal, though it has the physical properties of a non-metal.

Occurrence of sodium. Sodium is a widely distributed element, but because of its great chemical activity, especially toward oxygen and water, it is not found in the free state, but only in its compounds. Its compounds are all soluble in water, so they are largely found in sea water, as for example, common salt, or sodium chloride. This compound is the one used for preparing the metal. Chili saltpeter (NaNO<sub>3</sub>), borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) are also found in nature.

Preparation. Sodium was first made by Davy by the electrolysis of fused sodium hydroxide. Prior to this work sodium hydroxide was thought to be the element. The commercial preparation of sodium today utilizes the same method, in principle. A different source of electrical energy is used; electrical energy is now comparatively cheap, as it is generated by the dynamo, and particularly so if the dynamo is run by water power, as at Niagara Falls. Davy had to obtain his energy from a large battery of wet cells, making the method very expensive.

Sodium cannot be obtained by the electrolysis of its compounds in solution, because of the action of the element with water. The process in use at Niagara Falls was devised by Castner (page 174) and is as follows: Sodium hydroxide is melted and then becomes a conductor of the current, sodium being deposited at the cathode and oxygen escaping from the anode.

Prior to the generation of cheap electrical energy and its application to chemical industries, sodium was made by reducing sodium oxide with carbon. To bring about this reaction sodium carbonate was heated with carbon. This equation shows the reaction:

In reality this occurs in three steps:

 $Na_2CO_3$  heated $\rightarrow Na_2O+CO_2$   $Na_2O+C\rightarrow 2Na+CO$  $CO_2+C\rightarrow 2CO$ 

Properties and uses. Sodium is so active that it has no uses as an element. It is one of the strongest, or most active, metals and forms with water one of the strongest bases, sodium hydroxide (NaOH). With air the action is so great that it must be kept under kerosene (page 175). Sodium compounds impart a deep yellow color to a colorless or bluish flame, if a platinum wire is dipped into a solution containing them and then held in the flame. This serves as a test for the metal in its compounds.

Preparation of sodium hydroxide. As shown in the preceding paragraph, sodium hydroxide is obtained by the action of sodium on water. In its commercial preparation use is made of this reaction. The method consists of the electrolysis of a sodium chloride solution. The sodium discharged at the cathode reacts with the water to form sodium hydroxide. (See the description of the Townsend cell on page 176.) An older method consists of using moist lime (Ca(OH)<sub>2</sub>) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>). The equation is

## Na<sub>2</sub>CO<sub>3</sub>+Ca(OH)<sub>2</sub>→CaCO<sub>3</sub>+2NaOH

A variation of this method applied to potassium compounds formerly was a familiar farm-house operation. In the earlier days nearly every household made its own soap. Lye, either sodium hydroxide or potassium hydroxide, is necessary to act upon the fat and convert it into soap (see "Soap" in Lesson XVIII). To obtain this lye, wood ashes (preferably hardwood ashes) were treated with moist lime in a so-called "ash hopper," which was an inverted pyramid of rough boards lined with straw. Into this the mixed ashes and lime were put. Rain or added water promoted the reaction, the lye solution being collected as drippings at the bottom. Wood ashes contain potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), so the lye obtained was an impure solution of potassium hydroxide. It made a soft soap, while sodium hydroxide makes a hard soap.

Properties and uses. Sodium hydroxide is a white solid, very active and, therefore, hard to keep pure. It is a very strong base.

It has a corrosive action on animal and vegetable matter and is, therefore, called *caustic soda*. It is used where a strong base is necessary, in making soap, paper and dyes, in bleaching, and in refining kerosene oil.

#### **EXERCISES**

- 1. Describe the methods for preparing chlorine.
- 2. Give the physical properties of chlorine.
- 3. Discuss completely the chemical conduct of chlorine.
- 4. Give the uses of chlorine.
- 5. Explain nascent state. Give an example.
- 6. How is hydrogen chloride prepared?
- 7. Give the properties of hydrogen chloride.
- 8. What is the volume and the weight composition of hydrogen chloride? How are these facts determined?
  - 9. Discuss the properties of hydrochloric acid.
  - 10. Answer questions 1, 2, 4, 7, and 9, page 171.
  - 11. Solve problems 3, 5, 6, 8, and 10, page 171.
  - 12. What is a metal?
  - 13. Give the methods for preparing sodium.
  - 14. Describe the Castner process for making sodium.
  - 15. Give the properties of sodium.
  - 16. Give the chemical name and the formula for caustic soda.
  - 17. How is sodium hydroxide made?
  - 18. Discuss the properties and uses of sodium hydroxide.
  - 19. Solve problems 4, 5, 6, 7, and 9, page 178.
  - 20. Answer questions 8 and 10, page 178.
  - 21. How would you test for sodium compounds?

## LESSON X

## ACIDS, BASES, AND SALTS

# Assignment: Chapter XVI, McPherson and Henderson

Introduction. In the study of that branch of chemistry known as inorganic chemistry (it is with this branch that this course principally deals), the great majority of the compounds that can be studied belong to one of the groups known as acids, bases, and salts. Another important group is that of the oxides. Lavoisier considered oxygen to be a necessary constituent of an acid, as is evidenced by his naming the element "oxygen" (acid producer) and by his defining an acid as a compound of oxygen. We now recognize that in the case of such acids as hydrochloric acid oxygen is not present.

Oxides are closely related to both the bases and the acids. There are two kinds of oxides, oxides of metals and oxides of non-metals. Metallic oxides are related to bases as is shown by the following equation:

Non-metallic oxides are related to acids in a similar way:

$$SO_3+H_2O\rightarrow H_2SO_4$$

Sodium hydroxide (NaOH) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) are a base and an acid respectively.

The common acids. The word "acid" means a sour substance. The earliest acid known was acetic acid, which is the sour constituent in vinegar. The name "acetic" comes from the same word root, meaning sour. Acetic acid is formed from fruit juices by the action of certain bacteria, hence its early recognition. It is one of a large number of organic acids.

Just now we are more concerned with the inorganic acids, or mineral acids, as they are sometimes called. Common among these are hydrochloric (HCl), sulfuric (H<sub>2</sub>SO<sub>4</sub>), and nitric (HNO<sub>3</sub>) acids. These are usually used in water solution, and their acid properties are active only in solution. Generally, it is not necessary to make a distinction between the pure substance and its solution. Both are called acids.

Characteristics of acids. All acids have certain common properties. They all have a sour taste; they act upon certain organic substances to change the color (litmus is changed to a red color by acids); their solutions are conductors of the electric current, hydrogen being set free at the cathode. Certain metals have the power to liberate hydrogen from acids. Thus

and

$$Fe+H_2SO_4\rightarrow FeSO_4+H_2$$

Copper and some other metals will not liberate hydrogen. All acids will react with metallic hydroxides (bases) to form water and a salt, as shown by these equations:

 $NaOH+HNO_3\rightarrow HOH+NaNO_3$   $Fe(OH)_2+H_2SO_4\rightarrow 2HOH+FeSO_4$  $Cu(OH_2)+2HCl\rightarrow 2HOH+CuCl_2$  Properties of compounds are the result of the composition of the compounds. Since all acids contain hydrogen, it may be considered that these common properties are due to hydrogen. The properties are active only when the acid molecule is dissociated in solution; we may then assume further that the characteristic properties of acids are due to the presence of hydrogen ions (H<sup>+</sup>). An acid may be defined as a compound which, when in solution in a dissociating solvent, produces hydrogen ions.

Common bases. The common bases are frequently called alkalies. The word "alkali" originally meant ashes and was first applied to the ashes of sea plants. It is now applied to the hydroxides and carbonates of sodium, potassium, and sometimes to those of magnesium and calcium. The term "vegetable alkali" referred to the ashes of plants, which usually contained potassium compounds. The sodium compounds, obtained from rock salt, were called mineral alkalies.

The carbonates were formed in the ashes and were the first alkalies observed. As shown in Lesson IX, the carbonates treated with lime, that is, burnt limestone, are changed to the hydroxides. The hydroxides are much more active than the carbonates and have a stronger alkali action. The carbonates are called *mild alkalies*, while the hydroxides are called *caustic alkalies*. The hydroxides of sodium and potassium are commonly found in the grocery store under the names "soda lye" and "potash lye."

Characteristics of bases. Bases have a bitter taste, if soluble; they turn litmus blue; their solutions are conductors, a metal being discharged at the cathode and oxygen at the anode; they react with acids to form water and a salt. It is found that they all contain a metal and oxygen and hydrogen in the group known as hydroxyl (OH). They dissociate in solution to form a cation of the metal and an anion of the hydroxyl (OH). A base may be defined as a compound which, when in solution in a dissociating solvent, produces hydroxyl ions. The properties of bases, then, are due to the presence of these ions.

Undissociated acids and bases. These compounds in a perfectly dry state do not have the properties of acids and bases. Dry hydrogen chloride is not acted upon by zinc to form hydrogen. Hydrogen chloride, or hydrochloric-acid gas, dissolved in

benzene does not act with zinc to form hydrogen. Such a solution is not a conductor of the electric current. Benzene does not dissociate the hydrogen chloride molecules into ions and, hence, does not form a solution with acid properties. Similar statements apply to bases.

Neutralization. As shown under the properties of acids and bases, they react with each other to form water and a compound known as a salt. In this action the acid properties and basic properties are lost. If proper proportions of the acid and the base are used, the resulting mixture has neither a sour nor a bitter taste, turns litmus neither red nor blue. For this reason such a chemical reaction is called neutralization.

What really happens is that the hydrogen ion of the acid reacts with the hydroxyl ion of the base to form the undissociated molecule of water. The metallic ion of the base and the non-metallic ion of the acid remain ions, if the solution is dilute, or unite to form molecules, if the solution is more concentrated. These equations represent some neutralizations:

# $2KOH + H_2SO_4 \rightarrow 2HOH + K_2SO_4$ $Ca(OH)_2 + 2HCl \rightarrow 2HOH + CaCl_2$

Neutralization may be defined as the action of a base and an acid in which the cation of the acid unites with the anion of the base to form an undissociated molecule of water. The formation of the salt is a secondary step. Evaporation of the water permits the ions of the salt to come together to form molecules.

Neutralization, a definite act. Neutralization is a definite chemical action between base and acid compounds. Housewives are sometimes surprised that sugar does not sweeten a sour substance, while soda will. When milk sours, a definite acid known as lactic acid is formed. Sugar will not correct the unpleasant sour properties this gives to the milk. Soda will, for soda is a mild alkali, that is, it has basic properties; it corrects the sour taste of the milk by converting the lactic acid into water and a salt. Sugar, on the other hand, has no chemical action with the lactic acid. It leaves the lactic acid, and consequently the sour taste, in the milk. Large quantities of sugar may mask the sour taste, but not remove it.

The use of soda and sour milk in baking is an example of a similar nature. Here the purpose is to form carbon dioxide to raise the dough. The action must be between definite quantities of soda and sour milk. If not enough soda is used, the sour taste remains; if too much soda is used, the result is a bitter taste and a yellow color. The experiment described on pages 183 and 184 with solutions of acid and base of known concentration shows neutralization to be a definite chemical act. If 5 cc. of the acid solution requires 8 cc. of the base solution to neutralize it, then 10 cc. of the acid will require 16 cc. of the base, 20 cc. of the acid will require 48 cc. of the base to neutralize them.

Heat of neutralization. That the real chemical act in neutralization is the formation of water, and nothing but water, is shown by the examples given under this heading on page 184.

Salts. Sodium chloride is the commonest of all salts and gives the name "salt" to the group. Salts have a peculiar taste, which may be described as salty, but that does not mean the same as the taste of common salt. As a rule they have no action on litmus; their solutions are conductors; they are composed of a metal and a non-metal or a group of non-metal atoms. The following equations will show the formation of some salts:

 $Mg(OH)_2+2HCl\rightarrow 2HOH+MgCl_2$   $Zn(OH)_2+2HNO_3\rightarrow 2HOH+Zn(NO_3)_2$  $2Al(OH)_3+3H_2SO_4\rightarrow 6HOH+Al_2(SO_4)_3$ 

Salts are also formed when a metal replaces hydrogen:

 $2Al+6HCl\rightarrow 2AlCl_3+3H_2 \\ Mg+H_2SO_4\rightarrow MgSO_4+H_2$ 

The relation of salts to acids and bases is close. The salts contain the metal of the base and all of the acid except the hydrogen. A salt may be defined as a compound which is formed by the union of the cation of the base with the anion of the acid. Solutions of salts have no common ion.

Normal salts, acid salts, basic salts. A normal salt is one in which all of the hydrogen of the acid has been replaced by metal, and all of the hydroxyl of the base has been replaced by non-metallic ions, examples: NaCl, Na<sub>2</sub>SO<sub>4</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>. Evidently an acid

that contains only one hydrogen atom can form only a normal salt. One like sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) presents two possibilities. One or both of the hydrogen atoms may be replaced as follows:

$$NaOH + H_2SO_4 \rightarrow HOH + NaHSO_4$$
  
 $2NaOH + H_2SO_4 \rightarrow 2HOH + Na_2SO_4$ 

A compound like sodium hydrogen sulfate (NaHSO<sub>4</sub>) is called an acid salt. An acid salt may be defined as a salt which still contains a part of the hydrogen of the acid from which it is derived. Acid salts do not necessarily turn litmus red. Other reactions may cause an acid salt like baking soda (NaHCO<sub>3</sub>) to turn litmus blue.

A base which contains more than one hydroxyl group may form basic salts in like manner:

A basic salt is a salt which contains a part of the hydroxyl of the base from which it is derived. In solution acid salts and basic salts form ions characteristic of the acid or base as well as of the salt.

Strength of acids and bases. The strength of acids and bases must not be confused with the concentration of their solutions. Acid and basic properties are due to the presence of hydrogen and hydroxyl ions. That one will exhibit its characteristic properties to the greatest degree which dissociates the greatest percentage of its molecules into ions. Dissociation depends upon the nature of the compound and upon the concentration of the solution. In order to compare the strength of acids, their solutions must be taken of such concentration that they contain equivalent weights of hydrogen; for example, if a molar solution of hydrochloric acid is used, a half-molar solution of sulfuric acid must be used.

Conductivity measurements of such solutions show that the three common mineral acids are quite strong. In the order of strength, they are hydrochloric, nitric, and sulfuric. Other acids vary considerably in strength. Acetic acid is a weak acid. Bases in like manner vary considerably in strength. Potassium hydroxide is the strongest of the common bases, and sodium hydroxide comes next. Dilution of the solution increases the percentage of molecules which dissociate, but of course the actual number of

ions in a given volume is less as dilution is greater. Some substances dissociate in more than one way; take, for example, sulfuric acid, which forms the ions H<sup>+</sup> and HSO<sub>4</sub><sup>-</sup> in concentrated solution, and H<sup>+</sup>, H<sup>+</sup>, SO<sub>4</sub><sup>-</sup> in dilute solution.

Radicals. Groups of atoms like OH, SO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub>, and CO<sub>3</sub>, which are found in a number of related compounds and pass through chemical changes as a unit, are called *radicals*. The radicals of acids, bases, and salts become the ions upon dissociation. A radical is defined as a group of atoms acting as a unit in chemical change.

Nomenclature. The reader should refer to pages 189 and 190 for the methods used in naming acids, bases, and salts. It only needs to be added here that while all bases are hydroxides, all hydroxides are not bases. In fact all the oxygen acids are considered to be hydroxides. This is shown if we write the formulas as follows:

$$H_2SO_4 = (HO)_2SO_2$$
  
 $HNO_3 = HONO_2$ 

Electrochemical series. Reference has been made more than once to the fact that some metals, like zinc and iron, will replace hydrogen from acids, while others, like copper and silver, will not. Also, zinc will replace copper, lead, iron, and silver in solutions of their salts:

$$Zn+Pb(NO_3)_2 \rightarrow Pb+Zn(NO_3)_2$$

Copper will replace silver and mercury, but will have no effect upon solutions of salts of lead, iron, tin, and zinc.

A study of all the metals and hydrogen shows that they can be arranged in a series in the order of their ability to replace from solutions of their salts metals farther down the series. Study the table on page 191. This table of the metals indicates the order of their chemical activity. Those metals near the top form strong bases. Those above hydrogen will replace hydrogen from acids, while those below it will not.

#### **EXERCISES**

- 1. Give the characteristic properties of acids, bases, and salts.
- 2. Explain how acids and bases are related to oxides.
- 3. Define acid, base, salt, neutralization.

- $4.\ \,$  What is meant by a normal salt, acid salt, basic salt? Give examples.
  - 5. What is meant by the strength of an acid? What is a radical?
  - 6. What does the heat of neutralization show?
  - 7. Give the methods of naming acids, bases, and salts.
- 8. What is meant by the electrochemical series? Name ten metals in the correct order in this series.
- 9. What does the term "alkali" mean? What is soda lye; potash lye? Distinguish between caustic and mild alkali.
  - 10. Give examples to show that a dry acid does not have acid properties.
- 11. Give some examples to show that neutralization is a definite chemical action.
  - 12. Answer questions 3, 7, 8, 9, and 10, page 192.
  - 13. Solve problems 4, 5, and 6, page 192.

### SEND EXERCISES FOR LESSONS VI=X TO THE SCHOOL

### LESSON XI

# VALENCE; EQUATIONS

# Assignment: Chapter XVII, McPherson and Henderson

Definition of valence. A review of the formulas of some of the compounds studied in previous lessons will reveal the fact that all atoms do not hold in combination the same number of other atoms. One oxygen atom combines with two of sodium, but with only one of calcium, while two oxygen atoms combine with one of carbon. One atom each of chlorine, oxygen, nitrogen, and carbon combine respectively with one, two, three, and four of hydrogen.

Since one atom of hydrogen is never found in combination with more than one atom of some other kind, the hydrogen atom is taken as the basis for comparing the combining power of other atoms. This combining power, or combining value, is called valence. Valence may be defined as the property of an element which determines the number of hydrogen atoms its element will hold in combination. Elements which combine with one hydrogen atom are univalent, as shown in the formulas HCl, HBr. Bivalent elements are those that combine with two hydrogen atoms, as in formulas H<sub>2</sub>O, H<sub>2</sub>S. The formulas NH<sub>3</sub>, PH<sub>3</sub>, AsH<sub>3</sub> show trivalent elements. No element is known which has a valence higher than eight. Carbon is quadrivalent, as in CH<sub>4</sub>.

Construction of formulas. Elements which do not form compounds with hydrogen may be compared with chlorine, which is univalent, or with oxygen, which is bivalent, as in H<sub>2</sub>O. The oxides of many elements, then, are used to determine the valence of the element. If the formula of the oxide is found by experiment to be PbO, then the valence of lead is two. If we find it to be PbO<sub>2</sub>, the valence of lead is four. Elements which have the same valence, or valences which are multiples of each other, combine in a simple way. One atom of one element combines with one atom of the other, or one atom of one element combines with two atoms of the other, as in PbO and PbO<sub>2</sub> above.

But, if the valences are not multiples, but are two and three, for example, the formula for the compound must be constructed on the basis of the least common multiple. Phosphorus has a valence of three (PH<sub>3</sub>) and oxygen two (H<sub>2</sub>O). Each element in phosphorus oxide must be used a sufficient number of times to make the total valence of all atoms of each kind equal to the least common multiple of the two valences. In this case the least common multiple is six. Therefore, the formula for phosphorus oxide is  $P_2O_3$ . The rule to follow is: Take the least common multiple of the valences, divide the least common multiple by the valence, and the quotient is the number of times that atom is to be used in the formula.

Finding valence of elements. The valence of an element should not be found by referring to some table of valences, but by looking up some formula containing the element in the textbook, consulting the index to find the page where that element is described.

Suppose you wish to write the formula for bismuth sulfide. The index will refer you to page 362. Here you will find the formulas BiCl<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>, which show bismuth to be trivalent. Knowing the formula of hydrogen sulfide to be H<sub>2</sub>S, or finding it on page 233 if it is not known, sulfur is shown to be bivalent. The least common multiple would be six, and two atoms of bismuth and three of sulfur are necessary to form the compound bismuth sulfide, the formula for which is Bi<sub>2</sub>S<sub>3</sub>.

If the formula of a compound is known to be As<sub>2</sub>S<sub>5</sub>, the valences are found by the opposite procedure. The least common multiple of the number of both atoms is ten. The valence of

each element will be ten divided by the number of atoms of that element in the formula, or ten divided by two equals a valence of five for arsenic and ten divided by five equals a valence of two for sulfur.

Valence of radicals. When a compound consists of more than two elements, the above method for determining the valence of each element is not applicable. A more extended study of the chemical reactions is necessary to determine the manner in which the several elements are united to each other. Such a study is not possible here. Until such experimental evidence is at hand, we could make several guesses as to the valence of sulfur in sulfuric acid. See the structural formulas on page 196.

For our present purposes it is not necessary to know the valence of all the individual atoms. We are going to deal principally with acids, bases, and salts, which dissociate into cations and anions. These ions are of two kinds only, positive and negative. It is the valence of these parts, or radicals, of the molecule that we must know. The method described above for a compound of two elements like As<sub>2</sub>S<sub>5</sub> applies just as well to one composed of a metal and a negative radical, like Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. From this formula we could learn that iron is trivalent and the sulfate radical bivalent.

Finding barium to be bivalent from the formula BaCl<sub>2</sub> and the phosphate ion (PO<sub>4</sub>) to be trivalent from the formula H<sub>3</sub>PO<sub>4</sub>, we take the least common multiple, which is six, and dividing six by the valences, we get three barium atoms and two phosphate radicals to provide the total of six positive and six negative valences. The formula would be Ba<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. It is clear, then, that valence corresponds in number and kind to the charges which the ions carry when we are dealing with electrolytes.

Variable valence. The same element does not always have the same valence. When two elements form more than one compound, one or the other frequently has different valences. Iron forms two chlorides, having the formulas FeCl<sub>2</sub> and FeCl<sub>3</sub>. Assuming chlorine to have a valence of one in each case, iron is two in the former and three in the latter. Carbon has a valence of four in CO<sub>2</sub> and of two in CO, if oxygen is two in both cases.

This variation in valence need not confuse us. Ordinary chemical changes take place without change of valence. Only those changes that are oxidation and reduction reactions produce changes in valence. These cases will be pointed out as they are met with. Most elements have a dominant valence that more frequently occurs than the others. Thus carbon is usually quadrivalent, lead bivalent, and phosphorus pentavalent, rather than bivalent, quadrivalent, and trivalent respectively.

Equations. The valence of the elements can now be put to use to aid us in writing equations. As has been shown in an earlier lesson, the chemical equation is merely a representation of the facts of the reaction. These facts must always be determined either by laboratory experiment or by study of the results of the experiments of others.

Suppose we are required to write the equation representing the reaction in which aluminium hydroxide dissolves in sulfuric acid. A complete and original investigation of this reaction would involve an analysis of aluminium hydroxide and sulfuric acid to find formulas to represent their composition. It would be found that the formulas Al(OH)<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> represent these compounds. Then, the substances formed would have to be studied to find out their composition. It could be shown that water and aluminium sulfate are formed and that their formulas are H<sub>2</sub>O and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

Some of these steps can be predicted, instead of being actually determined by experiment, if we apply the knowledge we have gained of the principles of valence and the properties of compounds. It will be recognized that aluminium hydroxide, being a metallic hydroxide, is a base. Sulfuric acid will be recognized as an acid. From a knowledge of their properties, we know that they will act to form water and a salt, as all acids and bases will. If we are familiar with the formulas for other compounds of aluminium, we will learn that its atom has a valence of three. The formula for aluminium hydroxide would therefore be Al(OH)<sub>3</sub>, since the OH radical is always univalent. As sulfuric acid has the formula H<sub>2</sub>SO<sub>4</sub>, the SO<sub>4</sub> radical is bivalent. A temporary equation can now be constructed:

 $Al(OH)_3+H_2SO_4\rightarrow HOH+AlSO_4$ 

Now apply the valences to obtain the correct formulas on the right-hand side of the arrow. The valences give a least common multiple of six. The trivalent atom Al must, therefore, be used two times, and the bivalent radical SO<sub>4</sub> three times in the formula for aluminium sulfate. H<sub>2</sub>O or HOH is, of course, the correct formula for water. The equation now stands as

# $Al(OH)_3 + H_2SO_4 \rightarrow HOH + Al_2(SO_4)_3$

It remains to use as many of each of the above molecules as are necessary to give an equal number of all atoms on both sides of the equation. That is to say, the equation must be balanced. In balancing an equation the student must be careful not to change the formulas for any of the compounds. Those formulas represent the composition of the compounds as nature made them. The student must not take upon himself the supernatural power to change them. All he can do is to take more of the molecules. This is done by placing the proper coefficients in front of the formulas.

It is best to start at the left-hand side of the second temporary equation, as written above, and, taking each atom or radical in turn, count them on each side. Thus, we have one Al on the left and two on the right. Therefore, take two molecules of Al(OH)<sub>3</sub>. This gives us six OH radicals, and six molecules of water will be necessary on the right of the equation, since each HOH molecule contains one OH radical. Now, we have six hydrogen atoms, which will have to be obtained from three molecules of H<sub>2</sub>SO<sub>4</sub>. Putting three in front of H<sub>2</sub>SO<sub>4</sub> makes three SO<sub>4</sub> radicals, which we find already present in the one molecule of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> on the right of our equation. All parts having been tested and corrected, the complete equation is

# $2Al(OH)_3 + 3H_2SO_4 \rightarrow 6HOH + Al_2(SO_4)_3$

All double decomposition equations can be written by using the above method. When the products are not water and a salt, it must be known what they are. If a solid precipitates or a gas is formed, these substances can be recognized by tests. In the questions following this lesson, any reactions in which the products are not water and a salt will be described sufficiently so that the products will be known.

#### **EXERCISES\***

- 1. What is valence?
- 2. Give four kinds of valence and the formula of a compound to illustrate each.
- 3. Describe a method for finding the formula of a compound when the valences are known. Give an example.
- 4. How can you find the valence if you know the formula of a compound of the element? Give an example.
- 5. What is the connection between the valence of radicals and the electrical charges or ions?
- 6. Describe the steps in writing a double decomposition equation. Give an example.
  - 7. Give complete answers to all the exercises on page 199.
  - 8. Complete the following equations:

KOH+HNO₃→? KOH+H₂CO₃→? KOH+H₃PO₃→? Ba(OH)₂+HNO₃→? Ba(OH)₂+H₂CO₃→? Ba(OH)₂+H₃PO₃→? Cr(OH)₃+HNO₃→? Cr(OH)₃+H∘SO₄→?

9. Lead is sometimes quadrivalent. Write the formula for its hydroxide. Write the equation for the action of lead hydroxide with phosphoric acid (H<sub>2</sub>PO<sub>4</sub>).

 $Cr(OH)_3 + H_3PO_3 \longrightarrow ?$ 

10. From question 8 find the valence of chromium. Construct the formula for chromium sulfate. From question 2, page 199, find the valence of calcium. Chromium sulfate and calcium hydroxide precipitate chromium hydroxide. Write the equation.

## LESSON XII

## COMPOUNDS OF NITROGEN

# Assignment: Chapter XVIII, McPherson and Henderson

Reference was made in Lesson VII to the occurrence of compounds of nitrogen. Those parts of Lesson VII dealing with the occurrence and properties of nitrogen should be reviewed at this time. The chemical conduct of nitrogen compounds depends to a great extent upon the chemical properties of nitrogen. It was learned that nitrogen is a very inactive element. This may be

<sup>\*</sup>Prepare this set of Exercises and hold it until those for Lessons XII, XIII, XIV and XV are also prepared and then send all five sets to the School.

due to the great stability of the molecule of nitrogen, which has the formula N<sub>2</sub>, as we learn by the methods used in Lesson XVI.

Nitrogen has a tendency to leave its compounds to form the more stable nitrogen molecule, with the liberation of energy. Therefore, nitrogen compounds show a tendency to be unstable. Explosives are compounds of nitrogen which form a large volume of gas at the time of their decomposition. Compounds of nitrogen are numerous, but only those with hydrogen and oxygen need be studied here.

Ammonia. Three compounds of nitrogen and hydrogen are known. Ammonia (NH<sub>3</sub>) is the only one of sufficient importance to require discussion. It is formed by the decay or fermentation of organic matter containing nitrogen. For this reason the odor of ammonia is noticeable in stables, especially those occupied by horses, when the manure heats or ferments. It is sometimes called spirits of hartshorn, because it was first prepared by heating the horns of animals, such as deer or hart.

Commercial preparation. Practically all the ammonia used in this country is made by the destructive distillation of soft coal. The ammonia may be looked upon as a by-product of the process, but in reality there are four important products, coke, coal tar, ammonia, and coal gas. Soft coal is heated in retorts from which air is excluded, and a great variety of substances are obtained which belong in the four groups above named. The process is described on page 306.

The gases formed are passed through the liquids in the hydraulic main, where the ammonia and water form the ammoniacal liquor. Some more ammonia is dissolved by water in the scrubber. The ammoniacal liquor is treated with lime, and the pure ammonia distills over. It is dissolved in water or in dilute acid. Sulfuric acid is frequently used, as it is cheap and the ammonium sulfate formed can be used as a fertilizer.

Recently a process has been developed for making ammonia from the elements nitrogen and hydrogen. The reaction is an old one. The difficulty with it was that the ammonia decomposed almost as fast as it was formed. Haber succeeded in finding conditions under which this decomposition is retarded. The best yield is found when the mixture of gases is heated to 500° C.

under a pressure of 200 atmospheres. Finely divided iron is used as a catalytic agent. The ammonia formed is dissolved by water and the residual gases used over again (page 203). The method is used commercially in Germany as one of the ways for fixing nitrogen. Either ammonium sulfate for use as a fertilizer or nitric acid for use in making explosives is made from the ammonia.

Laboratory preparation. On a small scale or for laboratory purposes, ammonia is prepared from ammonium salts, such as ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) or ammonium chloride (NH<sub>4</sub>Cl), by treating them with a base, like sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)<sub>2</sub>). Ammonium hydroxide (NH<sub>4</sub>OH) is formed, which is unstable and decomposes to form ammonia and water. For a description of the method, see page 202. The reaction is a simple double decomposition in its first step:

# $NaOH+NH_4Cl\rightarrow NaCl+NH_4OH$ $NH_4OH\rightarrow NH_3+H_2O$

Properties. Consult page 203 for the physical properties of ammonia. Its odor is very striking and the gas can be unmistakingly recognized by the sense of smell. It is very soluble in water. The experiment described on page 170 in connection with hydrogen chloride works equally well with ammonia. The density of the ammonia solution is less than that of water as there is expansion when the gas is dissolved. The great solubility of ammonia may be partly explained by the fact that some of it combines chemically with the water.

The important chemical actions of ammonia are not many. Of greatest importance is the one with water just mentioned. Most of the common reactions which we think of in connection with ammonia are, in reality, the reactions of its compound with water, ammonium hydroxide. Other reactions of ammonia are: with metals, like magnesium, it will form nitrides, for example,  $(Mg_3N_2)$ ; and it will burn with oxygen at high temperatures.

Ammonium hydroxide. When water and ammonia combine, ammonium hydroxide (NH<sub>4</sub>OH) is formed. The solution is found to have basic properties, such as turning litmus blue and neutralizing acids. This can be so only if OH<sup>-</sup> ions are present in the

solution. The NH<sub>4</sub>OH molecule is supposed to be formed and to dissociate into NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup>. Ammonium hydroxide has never been separated from its solutions. The radical (NH<sub>4</sub>) forms the cation and otherwise has metallic properties; hence the name "ammonium" is given to it. A well-defined series of salts are formed with all the well-known acids, and these are called ammonium salts. Ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, ammonium chloride (NH<sub>4</sub>Cl), and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) are examples.

Uses. Ammonia is used for making ammonium salts, which are used in fertilizers. The expansion of liquid ammonia is utilized in making artificial ice (page 110).

Composition. The volume composition of ammonia is shown by decomposing a known volume of ammonia gas into hydrogen and nitrogen. It is found that 2 volumes of ammonia give 1 volume of nitrogen and 3 volumes of hydrogen.

Nitrogen acids. Of the nitrogen acids, nitric acid (HNO<sub>3</sub>) is by far the most important. Another is nitrous acid (HNO<sub>2</sub>), which is unstable and weak; its sodium salt is used in dye manufacture. These compounds do not occur in nature, but are made from other compounds.

Preparation of nitric acid. Most of the nitric acid used is made from sodium nitrate (NaNO<sub>3</sub>), commonly called Chili saltpeter. The method and the reaction are described on page 207. The salt is treated with concentrated sulfuric acid and heated gently; no reaction seems to take place, if the mixture is left cold. If dilute acid is used, mainly water distills off; but under proper conditions, nitric-acid vapor distills over and condenses. The explanation of this reaction will be taken up under the subject of equilibrium in the next lesson.

Depending upon the amount of sulfuric acid used, the reaction is represented in two ways. Usually sodium acid sulfate is formed, as in the following equation:

With less sulfuric acid and more heat, normal sodium sulfate is formed, but the higher temperature decomposes some of the nitric acid, so the process is wasteful:

$$2NaNO_3+H_2SO_4\rightarrow Na_2SO_4+2HNO_3$$

The same reactions are made use of in preparing nitric acid commercially as in the laboratory.

In order that the nitrogen of the atmosphere may be utilized to make nitric acid, other methods have been devised. One brings about the union of a part of the oxygen and the nitrogen of the air to form nitric oxide. This requires a high temperature, over 2000° C., which is produced by a magnified electric arc (Fig. 87, page 209). The oxide is passed into water, where a dilute solution of nitric acid is formed. The method is known as the Birkeland-Eyde process. The acid is neutralized with lime, forming calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>). This is known as air saltpeter and is used as a fertilizer.

Nitric acid can also be formed by the oxidation of ammonia in the presence of a catalyzer. These two methods were used during the war by Germany to make nitric acid, as they could not import Chili saltpeter, because of the naval blockade.

Properties of nitric acid. The physical properties of nitric acid are set forth sufficiently on page 209. Its chemical conduct may be best considered under two general kinds of chemical behavior: (1) as an acid; (2) as an oxidizing agent. Its behavior on heating and its action with metals belong under one or the other of these heads.

1. As an acid. Nitric acid is a strong acid, that is, in moderately dilute solutions it is highly ionized and conducts the electric current. It has a sour taste, turns litmus red, and neutralizes bases, forming salts called nitrates. With certain very strong metals and very dilute solutions of the acid, it can have its hydrogen replaced, thus:

# $Mg+2HNO_3\rightarrow Mg(NO_3)_2+H_2$

Ordinarily, however, any hydrogen that may be replaced is acted upon by other molecules of nitric acid, reduction products of nitric acid being formed (page 211).

2. As an oxidizing agent. Nitric acid is a strong oxidizing agent because of its easy decomposition. In the presence of reducing agents, the oxygen which is available for oxidizing purposes is shown by the following equation:

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The oxygen is enclosed in brackets to show that it is not actually set free. This oxygen will combine with the reducing agent, carbon, hydrogen, or a metal as follows:

$$C+2[O] \rightarrow CO_2$$
  
 $H_2+[O] \rightarrow H_2O$ 

With most metals the oxide, which is formed, is basic in its properties and combines with more nitric acid to form the nitrate of the metal. The action of metals above hydrogen in the electrochemical series, such as zinc or iron, is best represented as shown on page 211. For metals after hydrogen, such as copper or silver, the equation near the middle of page 212 best represents what takes place. In the decomposition of nitric acid on heating, we may imagine that it first decomposes in the same way as when it acts as an oxidizing agent, but that in the absence of a reducing agent some of the oxygen combines with the nitric oxide (NO) to form dioxide (NO<sub>2</sub>) as follows:

 $4HNO_3\rightarrow 2H_2O+4NO+6[O]$   $4NO+6[O]\rightarrow 4NO_2+O_2$  $4HNO_3\rightarrow 2H_2O+4NO_2+O_2$ 

Adding we have

which represents the final results of the action. Nitric acid will oxidize certain compounds by removing hydrogen from them. An example is the action between hydrochloric and nitric acids. These equations show the result of the action:

 $2HNO_3\rightarrow H_2O+2NO+3[O]$  $6HCl+3[O]\rightarrow 3H_2O+3Cl_2$ 

This mixture of acids is called *aqua regia* (page 213) because of its power to dissolve gold, the king of metals. It is the nascent chlorine that is the active agent.

Oxides of nitrogen. There are five oxides of nitrogen. Their names, formulas, and physical states are given in the table on page 214. Three can easily be prepared. Two, nitrogen trioxide and nitrogen pentoxide, are hard to make and are only important as they are related to nitrous and nitric acids. When added to water they combine according to the following equations:

 $N_2O_3+H_2O\rightarrow 2HNO_2$  $N_2O_5+H_2O\rightarrow 2HNO_3$ 

For this reason they are called acid anhydrides (page 217).

Anhydrides. The term "anhydride" may be given a broader application and made to include basic oxides as well as acid oxides (see "Introduction," Lesson X). An anhydride may be defined as an oxide which can be obtained from an acid or a base by the elimination of water. Examples of acid anhydrides and their acids are:  $SO_2 \rightarrow H_2SO_3$ ,  $Cl_2O \rightarrow 2HClO$ ,  $SO_3 \rightarrow H_2SO_4$ , and those given in the previous paragraph. Examples of basic anhydrides and their bases are:  $K_2O \rightarrow 2KOH$ ,  $Na_2O \rightarrow 2NaOH$ ,  $CaO \rightarrow Ca(OH)_2$ ,  $Fe_2O_3 \rightarrow 2Fe(OH)_3$ .

Nitrous oxides. Nitrous oxide is frequently called laughing gas and is used by dentists in extracting teeth, as it is a mild anesthetic. It is prepared by heating ammonium nitrate:

# $NH_4NO_3 \rightarrow 2H_2O + N_2O$

It will support combustion easily as it is sufficiently unstable to give up its oxygen.

Nitric oxide. Nitric oxide is made by the action of nitric acid on a metal; copper is usually used. The reactions are those given under nitric acid on page 212. It is a colorless gas which unites readily with oxygen to form nitrogen dioxide (NO<sub>2</sub>) (page 215). It is more stable than nitrous oxide and will not support the combustion of wood or sulfur, but it will support the combustion of phosphorus.

Nitrogen dioxide. Nitrogen dioxide can be made by decomposing nitrates (page 216). It is a brown gas with suffocating odor and is a poison. It gives up part of its oxygen and acts as an oxidizing agent.

#### **EXERCISES**

- 1. How was ammonia originally prepared?
- 2. Give the usual commercial method for making ammonia.
- 3. State the essentials of the Haber process for making ammonia.
- 4. Give the laboratory method for making ammonia. Give equations.
- 5. What property characterizes compounds of nitrogen?
- 6. Give the physical properties of ammonia.7. State the chemical reactions of ammonia.
- 8. What is the ammonium radical? Give its properties.
- 9. State the uses of ammonia.
- 10. What is the volume composition of ammonia?
- 11. Give the usual method for preparing nitric acid. Equations.
- 12. Give two other methods for making it. Describe the Birkeland-Eyde method.

- 13. What are the physical properties of nitric acid?
- 14. Give a full statement of the chemical properties of nitric acid.
- 15. Give name, formula, and a distinguishing property for the oxides of nitrogen.
  - 16. How is laughing gas made?
  - 17. Give its properties and uses.
  - 18. How are nitric oxide and nitrogen dioxide made?
- 19. Define anhydride. Give three examples each of acid and basic anhydrides.
  - 20. Write equations for the action of nitric acid on mercury.
  - 21. In what different ways do metals act on nitric acid?
  - 22. What is aqua regia? Write the equation for its action.
  - 23. Answer questions 1, 2, 3, 4, 5, 6, 7, and 8, page 217.
  - 24. Solve problems 14, 15, 16, 17, 18, and 19, page 218.
- 25. Give chemical name, formula, and use for air saltpeter, Chili saltpeter, and laughing gas.

## LESSON XIII

# EQUILIBRIUM; PERIODIC SYSTEM

#### **EQUILIBRIUM**

# Assignment: Chapter XIX, McPherson and Henderson

Speed of a reaction. Some reactions take place with a much greater velocity than others. Most inorganic reactions proceed very rapidly, while organic reactions are generally slow. However, iron rusts slowly. At ordinary temperature copper and oxygen combine slowly, and the action of pure zinc on sulfuric acid is very slow. By the speed of a reaction is meant the amount which undergoes change in a given time.

Besides the nature of the substance, three factors influence the velocity of a reaction.

- 1. Temperature. Raising the temperature promotes the speed of a reaction. Coal burns faster when the fire is hot. A metal acts faster with an acid if we heat it. Cold storage retards the chemical change of decay. "Pressure cookers," which give a temperature higher than usual for boiling water, shorten the time of cooking.
- 2. Concentration. It was seen that substances burn faster in pure oxygen than in air. Zinc will dissolve faster in concentrated hydrochloric acid than in dilute. Instead of increasing the concentration, the same result may be obtained by increasing the

surface of the reacting substances. Coal dust and oxygen combine so rapidly as to cause explosion at times. Kindling burns faster than the same wood in logs. An excess of one substance causes no more action, but it does cause it to go faster. Forcing air over coal will make it burn faster. The use of an excess of one substance is to produce the effect of mass action.

3. Catalysis. Sometimes certain substances can be added to a reaction and cause it to go faster or slower without seeming to take any part in it. At least, the added substance comes out of the reaction the same in kind and quantity as when it went in. These substances are called catalyzers, and the effect produced is known as catalysis. We have had examples in the preparation of oxygen (page 26) and of ammonia (page 203). Water is sometimes a catalyst; dry carbon monoxide (CO) will not burn. A class of substances, called enzymes, act by catalysis. Enzymes are formed by bacteria and promote such reactions as the splitting of cane sugar into dextrose and fructose, the fermenting of dextrose to alcohol, the souring of milk, and the decay of organic matter generally. Enzymes play an important part in the processes of digestion.

Reversible reactions. Several examples of reactions which will go in either direction according to conditions have already been met with. These are called reversible reactions. This property of the reaction may be represented by the double arrow in the equation.

 $3O_2 \rightleftharpoons 2O_3$  (page 114)  $2NH_3 \rightleftharpoons N_2 + 3H_2$  (page 203)  $2HgO \rightleftharpoons 2Hg + O_2$  (page 25)

Burning limestone gives lime and carbon dioxide, but lime will absorb carbon dioxide at ordinary temperatures:

Nearly all reactions are reversible, though not always in as simple a way as in the examples above.

Equilibrium. The reaction of steam and heated iron is a reversible reaction. The products, iron oxide and hydrogen, will form steam and iron:

If steam is passed over the iron and the hydrogen allowed to escape, the reaction goes from left to right. However, if we place iron oxide in the tube and pass hydrogen, the steam formed will escape and the reaction will go from right to left.

Now imagine the molecular equivalent amounts of iron and steam sealed up in the tube and the tube heated. At first the reaction will be mostly from left to right. As the iron and steam are used up, this reaction slows down. Meanwhile, the reaction between iron oxide and hydrogen has been gaining velocity, as these substances were formed in greater quantities. This will continue until the speed of the reverse reaction equals the speed of the original reaction. This point is called *chemical equilibrium*. This point will be reached when the molecular quantities used up in one direction are just offset by the molecular quantities of the same substances formed by the reaction in the other direction.

Chemical equilibrium is not to be considered as a state of rest, but, rather, as the balance between two opposite forces which exactly equal each other. If you are walking on a moving sidewalk in the opposite direction to which it is moving, but with the same speed, you appear at rest with reference to a lamp post by the side of the walk. It is possible to have all the substances involved in reversible reactions present together in equilibrium with each other. The average percentage of each material will then remain unchanged. In the formation of ammonia by the electric spark, equilibrium is reached when 7 per cent of ammonia is present.

Increasing the mass of a substance on the left or removing one of the products on the right will result in a change in the equilibrium. In the example above, if we add more steam, or remove the hydrogen, or do both, the reaction will go more nearly to completion. In general, a reversible reaction may be made to go to completion if one of the products of the reaction is removed as fast as it is formed.

Equilibrium in solution. Many of our most familiar and important reactions take place in solution. Here, we are concerned primarily with the equilibrium of ions with the molecules from which they are formed. Mixing the solutions of two com-

pletely dissociated electrolytes does not change the ionic condition; we have all four kinds of ions present. Most solutions do not completely dissociate their electrolytes. In such cases we have all four kinds of molecules present, as well as all four kinds of ions. Take sodium chloride and potassium nitrate:

The original solutions contain the molecules NaCl and KNO<sub>3</sub> and the ions Na<sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup> and NO<sub>3</sub><sup>-</sup>. When mixed, these ions form the molecules KCl and NaNO<sub>3</sub> as readily as the original NaCl and KNO<sub>3</sub>.

Completion of reactions in solutions. Such double decomposition reactions in solutions will go to completion only when one of the products is removed from the reaction. This may happen only if one of the following conditions is established.

1. A volatile gas may form. This includes cases where the product of the action is itself an insoluble gas or a very unstable substance like ammonium hydroxide which splits up to form a gas. Complete reaction results if conditions are changed so as to make a substance a gas which is not usually a gas or to prevent solution if the product is naturally soluble. The preparation of nitric acid is explained on this basis. The mixture was heated to make nitric acid a gas and concentrated sulfuric acid was used to prevent the solution of the nitric acid in water:

Other examples are:

 $2 \text{NaCl} + \text{H}_2 \text{SO}_4 \rightarrow \text{Na}_2 \text{SO}_4 + 2 \text{HCl}$   $\text{NaOH} + \text{NH}_4 \text{Cl} \rightarrow \text{NaCl} + \text{NH}_3 + \text{H}_2 \text{O}$   $\text{CaCO}_3 + 2 \text{HCl} \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2 \text{O}$ 

2. An insoluble solid may form. If an insoluble solid forms, the ions that form the insoluble molecule drop out of the solution as a precipitate and can take no part in the reverse reaction:

$$\begin{split} &\operatorname{AgNO_3} + \operatorname{HCl} \rightarrow \operatorname{\underline{AgCl}} + \operatorname{HNO_3} \\ &\operatorname{Pb}(\operatorname{NO_3})_2 + \operatorname{H_2SO_4} \rightarrow \operatorname{\underline{PbSO_4}} + 2\operatorname{HNO_3} \end{split}$$

The compounds underscored are the ones that precipitate. The others remain in solution partly ionized.

3. An undissociated molecule may form. The prominent example in this case is the reaction of an acid and a base. All acids and bases react to form an undissociated molecule of water (water is very slightly ionized). For examples consult Lesson X.

Hydrolysis. An example of a reversible reaction is the reaction of water with some salts. With a salt of a strong acid and base the reaction, NaCl+HOH→NaOH+HCl, is not noticeable because both sodium hydroxide and hydrochloric acid are strong and the tendency is altogether in the opposite direction. If either the acid or base formed is weak the result is different. In the case of

# Na<sub>2</sub>CO<sub>3</sub>+2HOH→2NaOH+H<sub>2</sub>CO<sub>3</sub>

the carbonic acid is weak. Its molecules do not form sufficient hydrogen ions to neutralize the hydroxyl ions of the base. Therefore, we have an excess of hydroxyl ions, and such a solution will turn litmus paper blue.

On the other hand, if the base formed is weak, the opposite result will be obtained. A solution of ferric chloride will turn litmus red:

# FeCl₃+3HOH→3HCl+Fe(OH)₃

The iron hydroxide is very weak, while the acid is strong. The reactions are called hydrolysis. Hydrolosis is the action of water upon a salt to form an acid and a base, one of which must be weak. If both acid and base are weak, the reaction may be complete hydrolysis. This is the case with aluminium carbonate and water:

$$Al_2(CO_3)_3 + 6HOH \rightarrow 2Al(OH)_3 + 3CO_2 + 3H_2O$$

This occurs in the use of alum baking powders, the alum first forming the aluminium carbonate.

#### PERIODIC SYSTEM

## Assignment: Chapter XXI, McPherson and Henderson

Classification of elements. It was early recognized that some relation existed between the atomic weights of elements and their properties. Döbereiner pointed out that several groups of three elements exist which were closely similar in properties and whose atomic weights were in arithmetical proportion. For example, chlorine, bromine, and iodine have quite similar properties.

The atomic weight of bromine is an approximate mean between those of chlorine and iodine:

 $35.46 + 126.92 \div 2 = 81.19$ . Bromine is 79.92

Again, a group calcium, strontium, and barium give similar results:

 $40.07 + 137.37 \div 2 = 88.72$ . Strontium is 87.63

These groups were called Döbereiner's triads.

The triads were incomplete, including only a part of the elements. In 1866 Newlands suggested his octaves. He arranged the elements in the order of increasing atomic weight, starting with hydrogen, and pointed out that every eighth element showed a similarity of properties. In 1869 Mendeléeff and Lothar Meyer brought out their periodic tables which are essentially the same and are a more complete elaboration of the idea of Newlands.

Periodic System. The table most frequently used and the one shown on page 258 is that of Mendeléeff brought up to date. Hydrogen is omitted as not having properties which properly place it with any of the groups. There are eight elements before properties begin to repeat. The elements found in any vertical column have marked similarity of properties. Lithium, sodium, potassium, etc., in Group I are much alike. So are fluorine, chlorine, bromium, and iodine in Group VII. Helium, neon, argon, etc., are placed in Group O because they were not known when Mendeléeff numbered the other groups.

It will be noticed that some elements in the same group are more similar to each other than they are to the others. Each group is therefore divided into two families. One family is placed to the left and the other to the right of the group. In Group I sodium should be placed with the left-hand group, as its properties are much more like those of lithium, potassium, rubidium, and caesium than they are like those of copper, silver, and gold. In Group VII fluorine had better be placed with the chlorine family.

It is seen that the properties of the elements do not vary continuously but repeat at regular intervals, or periods. The periodic law is stated thus: The properties of the elements are periodic functions of the atomic weights.

Uses of system. This arrangement of the elements has served to predict new elements. Mendeléeff predicted the existence of scandium, germanium, and gallium. The vacancies in the table may be filled by new discoveries. It has served to make possible a decision between two possible atomic weights for an element. But, for us, its most valuable use is that it simplifies study. A study of the properties of one element of a family will make easier the study of the others.

The physical as well as the chemical properties of the members of a family will be much the same. Members of the same family have the same valences. With hydrogen, the valence of the group increases from zero to four and then decreases. With oxygen there is an increase from zero to eight, though eight is not the common valence of the elements of Group VIII. In the following lessons we will study the elements in their families and point out in detail the application of the periodic law to the study of the properties of the elements.

#### **EXERCISES**

- 1. What is meant by the speed of a reaction?
- 2. Name the factors that influence speed. Give examples of each.
- 3. Define catalysis; enzyme. Give examples.
- 4. What is a reversible reaction? Give several examples.
- 5. Explain the effect of mass on the velocity of a reaction; on chemical equilibrium.
  - 6. Define chemical equilibrium. Give an example.
- 7. State the general condition necessary for a reversible reaction to go to completion.
- 8. State the condition of equilibrium in a mixed solution of two electrolytes, all substances being soluble.
- 9. Name three conditions under which a double decomposition reaction will go to completion in solution, using equations. Give two examples of each.
  - 10. Explain the preparation of nitric acid.
  - 11. Define hydrolysis. Give two examples.
  - 12. Answer questions 3, 4, 5, 6, and 9, pages 226 and 227.
  - 13. State the periodic law.
  - 14. What were Döbereiner's triads? Newlands' octaves?
  - 15. Briefly state the arrangement of the elements in the periodic table.
  - 16. What are the uses of the periodic system?
  - 17. Answer questions 1, 2, 5, and 6, page 263.

## LESSON XIV

## SULFUR AND ITS COMPOUNDS

Assignment: Chapter XX, McPherson and Henderson

Occurrence. Sulfur occurs both free and in the combined state. Free sulfur is found in two kinds of deposits in nature. Sulfur found in certain volcanic regions in Sicily and Japan until recently formed the world's principal supply. These deposits are formed from the gases emitted during an eruption; hydrogen sulfide (H<sub>2</sub>S) is present and is partially burned, the sulfur being deposited.

In the United States sulfur is found in Louisiana far underground. It is obtained by forcing superheated water into wells drilled into the deposits. This melts the sulfur, which is forced out of another pipe by compressed air. The liquid sulfur then solidifies. This source of sulfur now supplies the needs of this country and much is exported.

The sulfur deposits in Louisiana have an interesting origin. It is supposed that beds of calcium sulfate (gypsum) first existed. This was reduced to calcium sulfide by decaying organic matter. At the same time acids were formed which changed the calcium sulfide into hydrogen sulfide. Certain species of algae (a form of plant life) consumed the hydrogen sulfide, and, in the course of their life processes oxidized it to sulfuric acid. This in turn converted the calcium salts back to calcium sulfate. The cycle of sulfur was thus completed. But, the algae consumed more hydrogen sulfide than could be completely oxidized to sulfuric acid, and this surplus was changed to water and sulfur. The sulfur was stored up in the plant cells, much as other plants store up starch or animals store up fat. In the course of time these plants died, and their bodies decayed, leaving the deposit of sulfur.

Allotropic forms of sulfur. Four allotropic forms of sulfur are common; two of these are crystalline and two amorphous.

1. Rhombic sulfur. Rhombic sulfur is the ordinary form; brimstone is chiefly rhombic sulfur. This form is obtained by crystallizing sulfur from carbon disulfide solution. It appears as yellow plates usually with eight sides.

- 2. Monoclinic sulfur. When sulfur is melted and allowed to cool, monoclinic sulfur is obtained. The crystals are needle shaped. Rhombic sulfur changes to monoclinic sulfur above 95.5° C., which is known as the transition temperature; below this temperature the change is reversed.
- 3. Plastic sulfur. Plastic sulfur is amorphous and elastic, like rubber. It quickly passes into the rhombic form. It can be obtained by suddenly cooling sulfur in water.
- 4. "Flowers of sulfur." When sulfur first passes into the cold, some of it condenses to a fine crystalline powder, known as "flowers of sulfur."

These four forms are considered to be allotropic for the same reasons as those given for so considering the forms of carbon.

Properties and uses. The physical properties vary with the different forms. Sulfur burns to form a gas, sulfur dioxide (SO<sub>2</sub>). It will combine with most metals, forming sulfides. It is generally similar to oxygen in its chemical activity; it is not so active as oxygen is, but combines with about the same number of elements.

Sulfur is used in the manufacture of gunpowder, vulcanized rubber, lime sulfur spray, carbon disulfide, sulfur dioxide, and sulfuric acid. Lime sulfur spray is used as an insecticide for spraying fruit trees.

Hydrogen sulfide. This compound of hydrogen and sulfur is a disagreeable-smelling gas, the odor being suggestive of badly decayed eggs. It is formed in the decay of albuminous matter. It is found in volcanic gases and in certain waters, known as "sulfur waters." It can be made by the direct union of the two elements, but it is usually made from a metallic sulfide and an acid. Iron sulfide is used:

## FeS+2HCl→FeCl<sub>2</sub>+H<sub>2</sub>S

This reaction goes to completion because hydrogen sulfide is much less soluble in water than the hydrogen chloride. The water soon becomes saturated with hydrogen sulfide, and the excess of the gas escapes (page 233).

Properties of hydrogen sulfide. The physical properties of this substance can be studied on page 233. A study of its chemical conduct shows that its chemical properties can be best considered as of two kinds:

- 1. Acid properties. In water solution it is a weak acid. It is sometimes called hydrosulfuric acid. It has the properties of an acid, neutralizing bases, forming salts, and turning litmus red. Its salts are called sulfides.
- 2. Reducing action. Hydrogen sulfide is an unstable substance. When heated to 500° C., the speed of decomposition is very noticeable. Slow decomposition into hydrogen and sulfur takes place in solution. Because of this unstability it will react with metals below hydrogen in the electrochemical series, which, as an acid, it would not do. Silver is an example. Silver spoons and other tableware are tarnished black by the hydrogen sulfide in the air, especially when the cheaper grades of soft coal (which contain much sulfur) are burned. The ease with which hydrogen sulfide gives up hydrogen makes it a good reducing agent; the compound will combine readily with oxygen. With sufficient oxygen and high temperature we get

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

With less oxygen water and sulfur are formed:

$$2H_2S + O_2 \rightarrow 2H_2O + 2S$$

It will reduce certain oxidizing agents by taking the oxygen from them. With dilute nitric acid the action is shown thus:

$$2HNO_3 \rightarrow H_2O + 2NO + 3[O]$$
  
 $3H_2S + 3[O] \rightarrow 3H_2O + 3S$ 

Summing up the two steps we have

$$2HNO_3+3H_2S\rightarrow 4H_2O+2NO+3S$$

The sulfides. One of the principal uses of hydrogen sulfide is as a reagent to form sulfides of the metals. Most of the metallic sulfides are insoluble in water. The insoluble ones can be grouped into two classes: those insoluble in dilute acids, and those insoluble in alkaline solution. In this way the metals are divided into groups for the purposes of analysis. The sulfides which are insoluble can be prepared by passing hydrogen sulfide

through solutions of the salts of the proper metals. The soluble ones are made by neutralizing the proper base with hydrogen sulfide.

Sulfur dioxide. There are two oxides of sulfur, sulfur dioxide (SO<sub>2</sub>) and sulfur trioxide (SO<sub>3</sub>). They are the anhydrides of sulfurous acid (H<sub>2</sub>SO<sub>3</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Sulfur dioxide is the product of burning sulfur in oxygen; it has an irritating odor; under proper conditions it combines with oxygen to form sulfur trioxide; it may act as a reducing agent:

$$2H_2S+SO_2\rightarrow 2H_2O+3S$$

Sulfur dioxide combines with water to form sulfurous acid, and many of the reactions assigned to it are really the reactions of sulfurous acid (page 238).

Preparation of sulfur dioxide. It can be made in three ways:

- 1. Burning sulfur or a sulfide. The reaction is as follows:  $2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2$
- 2. Reducing sulfuric acid. The following equations show what happens:

$$H_2SO_4 \rightarrow H_2SO_3 + [O]$$
 $Cu + [O] \rightarrow CuO$ 
 $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$ 
 $H_2SO_3 \rightarrow H_2O + SO_2$ 

These steps give on addition

$$Cu+2H_2SO_4\rightarrow 2H_2O+SO_2+CuSO_4$$

3. Action of an acid on a sulfite. Sulfurous acid is first formed. It is unstable and breaks up to give water and sulfur dioxide:

$$Na_2SO_3+2HCl\rightarrow 2NaCl+H_2SO_3$$
  
 $H_2SO_3\rightarrow H_2O+SO_2$ 

This reaction would be reversible and establish equilibrium, except that the sulfurous acid decomposes as fast as it forms, giving sulfur dioxide, which, as a gas, escapes. For this reason the action is practically complete.

Sulfurous acid. Sulfurous acid is so unstable that it has never been isolated from the solution in which it is obtained when sulfur dioxide is passed into water. Some sulfurous acid molecules are formed and they ionize to form hydrogen ions. This is shown by the acid properties of the solution. Heating, however, drives off the sulfur dioxide, as if it were held in physical solution. Sulfurous acid has the properties of a weak acid and forms salts known as sulfites.

It is a reducing agent, having the power to take up another atom of oxygen to form sulfuric acid. It will reduce nitric acid:

 $2HNO_3\rightarrow H_2O+2NO+3[O]$  $3H_2SO_3+3[O]\rightarrow 3H_2SO_4$ 

or

# $2HNO_3+3H_2SO_3\rightarrow H_2O+2NO+3H_2SO_4$

It has bleaching and antiseptic properties and is used to bleach straw and flour. It is sometimes used as a preservative in certain foods. Calcium acid sulfite is used in paper manufacture (page 240).

Sulfur trioxide. Only traces of sulfur trioxide (SO<sub>3</sub>) are obtained when sulfur burns or when sulfur dioxide and oxygen are heated together. In order to get sulfur trioxide in quantity, a catalytic agent must be used. When sulfur dioxide and oxygen are passed over finely divided platinum at 400°, 98 per cent of the sulphur dioxide combines with oxygen (page 241). The principal use of sulfur trioxide is to make sulfuric acid by the contact process. It combines readily with water, forming the acid. For other properties see page 242.

Sulfuric acid. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) is one of the most important substances used by chemical industries. It is used in the manufacture of explosives, fertilizers, and dyes, in the refining of petroleum, and in the making of other acids. Sulfuric acid cannot be made in the manner that nitric and hydrochloric acids are made, because of its high boiling point.

Manufacture of sulfuric acid. Two methods for making sulfuric acid are in common use, the contact process and the lead-chamber process. The contact process is described on page 243. It is gradually being used in this country for the purpose of making concentrated sulfuric acid. The chamber process is the older method and is still used. A description of the process is found on pages 244, 245, and 246.

In studying, the student should recognize two distinct parts to the process: (1) the making of the acid, including the generation of sulfur dioxide and the introduction into the chambers of oxides of nitrogen, steam, and air and the reactions resulting; (2) that part of the process which is designed to save the oxides of nitrogen for repeated use. The Glover and Gay-Lussac towers, commonly called the hot and the cold towers, are used for the latter purpose, the oxides of nitrogen being dissolved in the cold tower and liberated in the hot tower, from which they pass with the sulfur dioxide into the lead chambers for use again.

This process gives an acid of about 65 per cent pure hydrogen sulfate. It is the cheaper method for making dilute sulfuric acid, while the contact process can compete with it in making the concentrated acid. Chamber acid can be concentrated by evaporation in platinum dishes.

Properties of sulfuric acid. Sulfuric acid is a heavy oil, sometimes called oil of vitriol. It has a high boiling point, 338° C. for the ordinary concentrated acid, which contains 2 per cent water (page 246). Its chemical behavior can best be discussed under four kinds of actions:

- 1. Acid properties. In water solution it is highly dissociated into ions and has the properties of a strong acid. It forms the ions H<sup>+</sup> and HSO<sup>-</sup><sub>4</sub> in concentrated solution and H<sup>+</sup>, H<sup>+</sup>, SO<sub>4</sub><sup>--</sup> in dilute solution. It reacts with bases to form normal salts (Na<sub>2</sub>SO<sub>4</sub>) and acid salts (NaHSO<sub>4</sub>). With metals above hydrogen in the electrochemical series, the dilute acid will act to form hydrogen and a sulfate of the metal.
- 2. Oxidizing action. When concentrated sulfuric acid is heated, it acts as a good oxidizing agent, like, but not so good as, nitric acid. One molecule of the acid will give up one atom of oxygen to combine with the reducing agent:

$$H_2SO_4 \rightarrow H_2O + SO_2 + [O]$$

The reducing agent may be carbon, hydrogen, a metal, or some compound. These equations show its action with carbon:

$$2H_2SO_4\rightarrow 2H_2O+2SO_2+2[O]$$
  
 $C+2[O]\rightarrow CO_2$ 

Adding, the final result is

$$2H_2SO_4+C\rightarrow 2H_2O+2SO_2+CO_2$$

Equations with copper are given on page 247. With aluminium and hot concentrated sulfuric acid, the following equations represent the action:

$$3H_2SO_4\rightarrow 3H_2O + 3SO_2 + 3[O]$$
  
 $2Al + 3[O] \rightarrow Al_2O_3$   
 $Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$ 

Combining these steps we have

$$2Al + 6H_2SO_4 \rightarrow 6H_2O + 3SO_2 + Al_2(SO_4)_4$$

- 3. Action with salts. This action depends upon the fact that sulfuric acid has a higher boiling point than the other common acids. When sulfuric acid is added to salts at a temperature above the boiling points of their acids, the acids escape as gases (page 225).
- 4. Action on water. Concentrated sulfuric acid is a good dehydrating agent because of its ability to combine readily with water. It is used as a drying agent because it will absorb moisture from gases that do not act with it.

Basicity of acids. Acids which form but one hydrogen ion will neutralize but one unit of a base and are called *monobasic* acids. Nitric acid (HNO<sub>3</sub>) is a monobasic acid. Acids, like sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), which form two hydrogen ions will neutralize two units of a base. They are called *dibasic* acids. We also have *tribasic* (H<sub>3</sub>PO<sub>4</sub>) and *tetrabasic* (H<sub>4</sub>SiO<sub>4</sub>) acids.

Carbon disulfide. Carbon disulfide is a heavy, disagreeable-smelling, colorless, oily liquid. It is said to have a pleasant odor when pure. It is used as a solvent for sulfur, rubber, gums, resins, and waxes. It is also used as an insecticide, its vapor being poisonous. It is made by heating carbon and sulfur together in an electric furnace (page 250).

Hydrates. The compounds which are formed when sulfuric acid, for example, combines with water are known as hydrates. Many salts have the property of combining with water in a similar way. Copper sulfate combines with five molecules of water to form the blue vitriol crystals (CuSO<sub>4</sub>.5H<sub>2</sub>O). Similarly we have such hydrates as Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O, BaCl<sub>2</sub>.2H<sub>2</sub>O, CaCl<sub>2</sub>.6H<sub>2</sub>O,

and FeSO<sub>4</sub>.7H<sub>2</sub>O. Such substances are true chemical compounds since they have a fixed percentage composition.

However, they are not very stable, but lose their water when heated slightly above the boiling point of water. Hydrates are compounds in which water molecules are held in a loose state of chemical combination with the main molecule. In dry air the water escapes at a lower temperature from some, like Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O. Such salts are said to effloresce. Efflorescence is the tendency of hydrates to lose water at ordinary temperatures. On the other hand, some salts, like calcium chloride (CaCl<sub>2</sub>), tend to absorb water from the air to form hydrates. They may even dissolve in the water and become liquid. They are said to deliquesce. Deliquescence is the tendency of salts to absorb water and become hydrates.

#### **EXERCISES**

- 1. Discuss the conditions under which sulfur occurs in nature. Explain its formation.
  - 2. Give the formation and properties of the allotropic forms of sulfur.
  - 3. State the chemical properties of sulfur.
  - 4. Name the uses of sulfur.
- 5. Give the occurrence and preparation of hydrogen sulfide. Give the equation.
- 6. Explain why the reaction for preparing hydrogen sulfide goes to completion.
  - 7. State the physical properties of hydrogen sulfide.
  - 8. What is hydrosulfuric acid? State its chemical properties.
  - 9. Write equations for three ways for preparing sulfur dioxide.
  - 10. Give the properties of sulfur dioxide.
  - 11. Discuss the properties of sulfurous acid.
  - 12. Give the preparation of sulfur trioxide.
  - 13. Describe the contact process for making sulfuric acid.
  - 14. Describe the lead-chamber process for making sulfuric acid.
  - 15. State the physical properties of sulfuric acid.
- 16. Discuss fully the four kinds of chemical properties of sulfuric acid, using equations to illustrate, when possible.
- 17. Define dibasic acid, tribasic acid, hydrate, deliquescence, efflorescence. Give an example of each.
  - 18. How is carbon disulfide made? Give its properties and uses.
  - 19. Complete the following equations:

Cu+hot concentrated  $H_2SO_4 \rightarrow ?$  ZnS+HCl $\rightarrow ?$  Cu+dilute  $H_2SO_4 \rightarrow ?$  Cu+dilute  $H_2SO_4 \rightarrow ?$  H<sub>2</sub>S+excess  $O_2 \rightarrow ?$  H<sub>2</sub>S+excess  $O_2 \rightarrow ?$  H<sub>2</sub>S+SO<sub>2</sub> $\rightarrow ?$  H<sub>2</sub>S+HNO<sub>3</sub> $\rightarrow ?$ 

- 20. Answer questions 1, 2, 3, 4, 5, 6, 7, 8, and 9, page 252.
- 21. Solve problems 11, 12, 13, 14, and 17, page 253.

#### LESSON XV

#### THE HALOGEN FAMILY

Assignment: Chapter XXII and Review of Chapter XIV, McPherson and Henderson

The family. The four elements, fluorine, chlorine, bromine, and iodine are placed in the second family of Group VII of the periodic table. They offer a good opportunity to observe the way in which members of the same periodic family both resemble and differ from each other. It will be noted that they differ only in the degree of their action, and not in the kind.

Furthermore, their properties, physical and chemical, are in direct relation to their atomic weights. They are called halogens because they are found mostly in combination as salts in sea water. The word "halogen" means salt former. They do not occur in the free state because they are so active chemically that if ever liberated as free elements, they always find some other element to combine with.

Physical properties. The table at the top of page 264 shows the principal physical properties of these elements. Note that there is an increase in melting point, in boiling point, and in darkness of color as the atomic weight becomes larger. Fluorine is a pale-yellow gas, chlorine a greenish-yellow gas, bromine a red liquid easily volatile, and iodine a black solid easily converted to a purple vapor.

Chemical Conduct. These elements are found in the last regular group of the periodic table, far removed from the strong metals. If the electrochemical series should be extended to include the non-metals, the halogens, with oxygen, would be found at the very end. Therefore, they are strongly negative elements in their chemical behavior, in fact, the most active of all the elements in a negative way.

As negative elements the halogens have properties similar to those of oxygen. For this reason they are very good oxidizing agents. The term "oxidation" must be thought of in a broader sense than in connection with oxygen alone; an oxidizing element is one with properties similar to oxygen. In this sense the halogen

elements are very active oxidizing agents. Sometimes they remove hydrogen from water, freeing the oxygen, in which reaction they are indirect oxidizing agents (see "Bleaching action," page 164); other times they oxidize directly, as:

It needs to be emphatically stated that all four of the halogen elements are good oxidizing agents. Some, however, are better than others. Their power as oxidizing agents, as well as their general chemical activity, varies inversely with their increasing atomic weights. Fluorine is most active, chlorine next, bromine next, and iodine least active as an oxidizing agent. Their tendency to form compounds with hydrogen and the metals varies in the same order. So does their bleaching action. With the other negative, or non-metallic, elements the halogens form less stable compounds. With oxygen only chlorine and iodine form compounds, and these are very unstable. Sometimes one halogen forms compounds with another halogen, but such compounds are very unstable.

Compounds with hydrogen. All the halogen elements form compounds with hydrogen in which they have a valence of one. The hydrogen compounds, in water solution, are all acids and form a series of salts in which the halogens combine with a valence of one with the metals, forming fluorides, chlorides, bromides, and iodides. The halogen hydrides vary in stability as the activity of the halogen itself varies; that is, the more active element will form the more stable hydride. In the order of their stability they are: hydrogen fluoride, hydrogen chloride, hydrogen bromide, and hydrogen iodide.

Since they are sufficiently unstable to give up their hydrogen under suitable conditions, these hydrogen compounds of the halogens are all reducing agents, some better than others. The best reducing agent is hydrogen iodide, the one with the largest molecular weight and the least stability, iodine being the least active halogen. Then comes hydrogen bromide, which is a better reducing agent than hydrogen chloride. It must be emphasized here that it is the hydrogen compounds of the halogens which act as reducing agents, the halogen elements being oxidizing agents.

Hydriodic acid and hydrobromic acid will reduce both nitric and sulfuric acids, hydriodic acid carrying the reduction of sulfuric acid, at least in part, to sulfur and hydrogen sulfide, while hydrobromic acid reduces it only to sulfur dioxide. Hydrochloric acid will reduce nitric acid (see the discussion of aqua regia in Lesson XII) but will not reduce sulfuric acid (see the discussion of the preparation of hydrogen chloride and hydrochloric acid in Lesson IX). Because of the action of hydriodic and hydrobromic acids on sulfuric acid, the latter cannot be used in preparing them (pages 270 and 274).

Fluorine. Because of its great activity, all early attempts to prepare fluorine failed. It is so active that it decomposes water; electrolysis of water solutions of its salts gives oxygen at the anode instead of fluorine. In 1886 Moissan prepared it by the electrolysis of a solution of potassium hydrogen fluoride (KHF<sub>2</sub>) in liquid hydrogen fluoride. A platinum or copper tube must be used, as the element decomposes glass. (See Fig. 104, page 267, and page 265.) The properties of fluorine will be understood from a study of the previous sections of this lesson. It unites with most elements, giving light, but the action with gold, platinum, or copper is superficial. It does not combine with oxygen.

Hydrofluoric acid. Hydrogen fluoride, or hydrofluoric acid, (H<sub>2</sub>F<sub>2</sub>) is prepared from calcium fluoride and sulfuric acid:

This action is completed because the acid is formed as a gas (page 267). Hydrofluoric acid is a weak acid, its water-insoluble salts being soluble in the strong acids. It acts vigorously upon organic matter and will produce a very painful and slow-healing sore when it comes in contact with the flesh. Glass is decomposed by it. Considering glass as partly composed of silicon dioxide (SiO<sub>2</sub>) the reaction is represented thus:

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O$$

The silicon tetrafluoride (SiF<sub>4</sub>) is a gas, which accounts for the completeness of the reaction. The acid must be kept in wax bottles. It is used in etching designs upon glass and china (page 268) and in decomposing silicates for analysis.

Chlorine. Chlorine and its compounds have been studied in Lesson IX. The first part of that lesson should be reviewed as a part of the work at this time.

Bromine. Bromine is found almost entirely in the form of sodium bromide (NaBr) and magnesium bromide (MgBr<sub>2</sub>), which are found in many salt waters. The word "bromine" means a stench, referring to the disagreeable odor of the element. It is one of the two liquid elements, the other being mercury. It can be prepared from its salts by the action of manganese dioxide (MnO<sub>2</sub>) and sulfuric acid. The complete equation is

$$2NaBr + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Br_2$$

Commercially, bromine is obtained by the electrolysis of salt water. If chlorine is set free in the process, it acts on the bromide to form bromine as follows:

This is because chlorine is more active than bromine and will liberate it from its compounds, just as zinc will liberate hydrogen or copper from their compounds. Bromine acts much like chlorine but is less active. It is used in preparing bromides and certain organic compounds as drugs and dyes.

Hydrobromic acid. Hydrogen bromide, or hydrobromic acid, cannot be prepared pure, as hydrochloric acid can, by the action of sulfuric acid on its salts. This is because the sulfuric acid oxidizes the hydrobromic acid which is first formed:

Hydrobromic acid is a better reducing agent than hydrochloric acid so it reduces the sulfuric acid, forming bromine (page 270):

$$H_2SO_4+2HBr\rightarrow 2H_2O+SO_2+Br_2$$

Hydrobromic acid can be made pure by two methods: (1) by the action of water, bromine, and red phosphorus as described on page 271; (2) by the action of hydrogen sulfide on bromine water as described for the preparation of hydriodic acid on page 274. Both these methods are suitable for preparing both hydrobromic and hydriodic acids. Except that it is less stable and a better reducing agent, the properties of hydrobromic acid are similar to those of hydrochloric acid.

lodine. The element iodine is obtained indirectly from sea water, either from the ashes of sea weeds or from the residues from which Chili saltpeter has been separated. The methods given for preparing chlorine and bromine by using manganese dioxide and sulfuric acid can be used here (page 269). Chlorine will liberate it from sodium iodide:

Commercially, it is now obtained from sodium iodate (NaIO<sub>3</sub>), which occurs in crude Chili saltpeter. It is liberated by the action of sulfites of sodium (page 273).

Iodine forms purplish-black crystals which give a brilliant purple vapor. Its odor is irritating but less so than those of bromine and chlorine. It can be set free from its salts by either bromine or chlorine:

$$2NaI+Br_2\rightarrow 2NaBr+I_2$$
  
 $2NaI+Cl_2\rightarrow 2NaCl+I_2$ 

It gives a bright blue color with starch solution, which serves as a test either for starch or for iodine as occasion requires. Tincture of iodine, a solution of iodine in alcohol, is used as a counter irritant in medicine. It is used to prepare iodides, dyes, and drugs. Iodoform (CHI<sub>3</sub>) is used as an antiseptic.

Hydriodic acid. This acid must be prepared by the methods given previously for the preparation of hydrobromic acid (pages 270 and 274). It is quite unstable and reacts with the oxygen of the air to free iodine:

$$4HI+O_2\rightarrow 2H_2O+2I_2$$

This causes the solution of hydriodic acid to turn brown on standing. It is a very strong reducing agent because of the ease with which it is decomposed into its elements. Its reactions in reducing sulfuric acid are represented as follows:

$$H_2SO_4 \rightarrow H_2O + SO_2 + [O]$$
  
 $2HI + [O] \rightarrow H_2O + I_2$   
 $SO_2 + 4HI \rightarrow S + 2I_2 + 2H_2O$   
 $S + 2HI \rightarrow H_2S + I_2$ 

Sulfur dioxide, sulfur, and hydrogen sulfide are all among the products formed in the action.

Salts of the halogens. The salts of the halogen acids are generally soluble in water. Exceptions are the chlorides, bromides and iodides of lead, silver, and mercurous mercury. Silver salts are used in photography because of their action toward light. Bromides and iodides of potassium are used in medicine. Sodium chloride is common table salt. Fluorite, fluor spar, or calcium fluoride (CaF<sub>2</sub>), is the most common fluoride.

Oxygen Compounds. These compounds are not numerous, as the halogens have little tendency to combine with oxygen, only chlorine and iodine doing so. Chlorine forms three oxides, having the formulas, Cl<sub>2</sub>O, Cl<sub>2</sub>O<sub>7</sub>, and ClO<sub>2</sub>, and four oxygen acids, HClO, HClO<sub>2</sub>, HClO<sub>3</sub>, and HClO<sub>4</sub>. In these compounds the valence of chlorine varies on the odd numbers from one to seven. These compounds are very unstable and are not important in themselves. The salts of hypochlorous acid (HClO) and of chloric acid (HClO<sub>3</sub>) are of some importance. Hypochlorites are good oxidizing agents and are used for bleaching and disinfecting purposes, as in the purification of water. The chlorates give up oxygen easily and are used in the manufacture of explosives and fireworks and in preparing oxygen. Hypochlorites and chlorates can be prepared from chlorine and the hydroxide of an alkali metal and also by electrolytic methods (page 276).

#### **EXERCISES**

- 1. Name the halogen elements in the order of increasing atomic weights.
  - 2. What does halogen mean?
  - 3. Compare the physical properties of the halogen elements.
- 4. Write a full discussion of the chemical conduct of the halogens as a family.
- 5. In what sense are they oxidizing agents? Give the order of their oxidizing power.
- 6. What kinds of reagents are their hydrogen compounds? Why? Name them in order from best to poorest.
  - 7. How is fluorine made?
  - 8. Give the properties of fluorine.
  - 9. Give the method for making hydrofluoric acid. Give the equation.
  - 10. Give the properties of hydrofluoric acid.
  - 11. Describe the method for etching glass.
  - 12. How is bromine made? Give the equations.
  - 13. State the properties and chemical conduct of bromine.
    14. How is hydrobromic acid made?

- 15. Write equations for the action of KBr upon H<sub>2</sub>SO<sub>4</sub>.
- 16. Give the properties, physical and chemical, of hydrobromic acid.
- 17. How is iodine made?
- 18. State all its properties.
- 19. Give the sources of all the halogen elements.
- 20. How is hydriodic acid made?
- 21. Give the properties of hydriodic acid.
- 22. Write equations for the action of H<sub>2</sub>SO<sub>4</sub> and NaI.
- 23. Name the water-insoluble halogen salts.
- 24. Give the method for preparing hypochlorites and their uses.
- 25. Give the methods for preparing chlorates and their uses.
- 26. Answer questions 1, 2, 3, 6, 8, 9, 12, and 13, pages 277 and 278.
- 27. Solve problems 15, 16, 17, and 18, page 278.

#### SEND EXERCISES FOR LESSONS XI=XV TO THE SCHOOL

## LESSON XVI

## MOLECULAR WEIGHTS; ATOMIC WEIGHTS

# Assignment: Chapter XXIII, McPherson and Henderson.

Chemical laws. Any attempt to find the atomic weights of the elements must be based upon the laws of chemical action. These have been studied in previous lessons. They are the laws of conservation of mass (Lesson I), of definite composition (Lesson II), of multiple proportion (Lesson IV), and of combining weights (Lesson V). From these laws the theory of the atom was deduced. These laws should be reviewed before proceeding farther with this lesson. It is recalled that to every element a number (determined by experiment) may be assigned which represents its combining, or equivalent, weight with every other element. The number selected will depend upon the element taken as a basis of comparison and the number given to it for a standard value.

Definition of equivalent weight. The natural selection for a standard would be 1 gm. of hydrogen, since hydrogen is the lightest element. Hydrogen, however, combines with a limited number of elements. Oxygen, on the other hand, combines with nearly all the elements. For convenience, it is usual to make a comparison between the weights of the different elements and a weight of oxygen with which they combine.

What number shall we assign to oxygen? If we use 1 gm. for oxygen, several elements will have combining, or equivalent, weights less than 1, which would be inconvenient. We might select 10, 12, 16, 50, or 100 as the weight of oxygen to use as a standard. Any of these numbers could be used and by an analysis of compounds of oxygen numbers could be found showing the weights of each which would combine with 10, or 12, or 16 gms. of oxygen.

To have a logical foundation for our standard, it seems best to take water, a compound of oxygen and hydrogen, which has been analyzed with the highest degree of accuracy. This gives a comparison between hydrogen, the natural standard, and oxygen, the convenient standard. When the composition of water is determined, we find 1 gm. of hydrogen combining with 7.94 gms. of oxygen or, to use a whole number of oxygen, 1.008 gms. of hydrogen combines with 8 gms. of oxygen. These numbers are directly determined from experiment. It is best, then, to use 8 gms. of oxygen as the standard of equivalent, or combining, weights rather than any other number. The equivalent weight of an element is defined as that weight of an element in grams which combines with, or is equivalent to, 8 gms. of oxygen.

Equivalents not atomic weights. The simplest thing would be to call the equivalent weights the atomic weights. This is apparently impossible, when the facts expressed by the law of multiple proportion are considered. Many elements are found to combine with several different quantities of oxygen; carbon with two, copper with two, iron with three, and nitrogen with five are examples. In these cases we are unable to decide which value truly represents the weight of the atom relative to the atom of oxygen.

Our problem must be attacked from another angle. The determination of the equivalent weight is, however, the first step in finding the atomic weight of any element. The equivalent weight can be determined with a much greater degree of accuracy than is possible with the other values to be found and serves to correct the final result.

Molecular weights. It is possible to decide which of the several equivalent weights of an element, or what multiple of an

equivalent weight, represents the true atomic weight if we can learn the molecular weights of the compounds of the element and the number of atoms in these compounds.

Our knowledge of molecules is largely obtained from the study of matter in the gaseous state. It is necessary, then, to review the gas laws of Boyle and Gay-Lussac and the kinetic theory explaining them (see Lesson III in this text and pages 60 and 61 in McPherson and Henderson). From the kinetic theory the hypothesis of Avogadro was derived. This states that under like conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules. Accepting this as true, and it has had a very thorough testing out in the development of the science, we have a method for finding the molecular weights of gaseous compounds, by comparing the weights of equal volumes.

Example. One liter of oxygen weighs 1.43 gms., 1 liter of carbon dioxide weighs 1.98 gms.; all the molecules in 1 liter of oxygen weigh 1.43 gms.; all in 1 liter of carbon dioxide weigh 1.98 gms. The weights of each molecule of the two gases are to each other as 1.43 is to 1.98. The molecular weight of carbon dioxide equals  $1.98 \div 1.43 \times$  the molecular weight of oxygen.

Molecular weight of oxygen. The number to be used as the molecular weight of oxygen must now be decided. It will depend upon the number selected as the atomic weight of oxygen, which may or may not be 8 as we shall see, and upon the number of atoms in a molecule of oxygen. Again it will be necessary to study the composition of water. This time its volume composition to form water vapor should be recalled (pages 78-79).

Gay-Lussac's law of combining volumes of gases. Other gases combining to form a gaseous product show a similar simple ratio between the volumes involved. Two volumes of hydrogen and 1 volume of oxygen form 2 volumes of water vapor, 3 of hydrogen and 1 of nitrogen form 2 of ammonia, and 1 of hydrogen and 1 of chlorine form 2 of hydrogen chloride. The law of combining volumes of gases states that when gases combine to form gaseous products, there is a small whole-number ratio between the volumes of the reacting substances and the volume of the product.

Formula of oxygen and water. Applying Avogadro's hypothesis to the volume composition of water and representing the equal volumes by squares, we have

$$H$$
  $H$   $+$   $O$   $\rightarrow$   $A$  water vapor

If equal volumes contain equal numbers of molecules, we have twice as many molecules of water vapor as we have molecules of oxygen. Every molecule of water vapor must contain at least one atom of oxygen. A complete study of other oxygen compounds would reveal no compound of oxygen containing less volume of oxygen than water. By definition of an atom, this quantity of oxygen must represent one atom of oxygen. Therefore, having one atom in each molecule, we have twice as many atoms of oxygen as we have molecules of oxygen. Oxygen molecules must, then, contain two atoms each and the formula for oxygen is O<sub>2</sub>.

If an examination of other hydrogen compounds should show none with less volume of hydrogen than water vapor, then each molecule of water vapor would contain one atom of hydrogen, and we would have the same number of atoms of hydrogen as we have molecules of hydrogen, and each molecule of hydrogen would contain one atom. The formula for water vapor would be taken as HO, and we could conveniently use 8 as the atomic weight of oxygen and 1.008 for that of hydrogen.

However, we would not examine hydrogen compounds long before studying hydrogen chloride. Its volume composition is represented as follows:

$$H$$
 +  $Cl$   $\rightarrow$   $D$  hydrogen chloride

Hydrogen chloride must contain at least one atom of hydrogen per molecule. A study of other hydrogen compounds shows none containing less hydrogen, therefore, hydrogen chloride does contain one atom of hydrogen per molecule. But this gives us twice as many atoms of hydrogen as we have molecules of hydrogen. Therefore, there must be two atoms in each molecule of hydrogen.

This being the case, we will have to revise our conclusion about water vapor, in which we found hydrogen indicated to have

one atom per molecule, since all hydrogen is exactly like all other hydrogen, there being no allotropic forms of hydrogen. If hydrogen contains two atoms in each molecule, in the two volumes of hydrogen used to form two volumes of water vapor we will have twice as many atoms of hydrogen as molecules of hydrogen and, therefore, twice as many atoms of hydrogen as molecules of water vapor, since the water vapor and the hydrogen molecules are equal in number. Each molecule of water vapor must, therefore, contain two atoms of hydrogen. The formula for water vapor must be  $H_2O$  and not HO.

Now, if we try to fit the experimentally determined weight ratio of hydrogen and oxygen to this formula, 1.008 gms. of hydrogen stands for two atoms and 8 gms. of oxygen for one atom. A single atom of hydrogen would have an atomic weight of little over one-half. This is an inconvenient value to use and, to avoid it, chemists have doubled the values in the above ratio, taking 16 to represent the weight of one atom of oxygen and 2.016 for the two atoms of hydrogen. In this way 16 becomes the atomic weight of oxygen and 1.008, the atomic weight of hydrogen. With two atoms in a molecule of oxygen, 32 is the molecular weight of oxygen.

Gram-molecular volume. Referring again to the example of carbon dioxide and recalling that 1 liter of oxygen weighs 1.43 gms. and 1 liter of carbon dioxide weighs 1.98 gms., the molecular weight of carbon dioxide would be found by the proportion

$$1.43 : 1.98 : : 32 : X$$
 $X = \frac{1.98 \times 32}{1.43} = 44$ 

But

$$32 \div 1.43 = 22.4$$

Therefore, in any case the weight of a liter of the gas multiplied by 22.4 equals the molecular weight of the gas; for oxygen:

$$1.43 \times 22.4 = 32$$

In other words, 32 grams of oxygen would occupy 22.4 liters under standard conditions. The molecular weight of any other gaseous compound in grams will occupy this same volume (22.4)

liters) under standard conditions. This is called the gram-molecular volume.

Finding the atomic weight. The second step in finding the atomic weight of an element is to multiply the weights of 1 liter of all its gaseous compounds by 22.4 to find their molecular weights. Third, the per cent of the element whose atomic weight is to be found must be determined in all the above compounds. Fourth, multiply the molecular weight by the per cent of the element in the compound, and we have a value representing the weight of all the atoms of that element which the compound contains. It will be found that these values group themselves around certain points, the larger ones being approximate multiples of the smallest group. This means that those compounds containing the small amounts of the element contain one atom, since we find no compound to contain less. This smallest number does not agree exactly with other values in its group because of experimental errors in finding the weights of one liter of the several gases. The larger values show two, three, or four atoms, as the case may be, to be contained by the compounds from which they are derived. Fifth, the exact atomic weight of the element is found by multiplying the equivalent weight, previously determined, by some small whole number which will bring it into approximate agreement with the above approximate atomic weight. The product thus obtained is the exact atomic weight. See the calculation of the atomic weight of nitrogen as worked out on pages 286 and 287.

Other methods of determining molecular weights. So far we have considered only those compounds which are gases. Other methods are useful in studying compounds which are not gases, but they are of limited application. From Raoult's laws (page 285), the molecular weight of substances which dissolve without ionic dissociation may be found by finding the lowering of the freezing point, or the rise in the boiling point, produced by the dissolved substance.

Molecular formula. In Lesson V a method for finding the simplest percentage formula was given. It is now possible to find the correct molecular formula for a compound, if we know its molecular weight.

Example. The molecular weight of a compound is 78, it contains 7.7 per cent hydrogen and 92.3 per cent carbon. Find the molecular formula.

 $78 \times 0.923 = 71.99$ , part of molecular weight due to carbon  $78 \times 0.077 = 6.006$ , part of molecular weight due to hydrogen

These weights divided by the atomic weights of carbon and of hydrogen will give the number of atoms of each element in the compound.

 $71.99 \div 12 = 5.999$ , or 6 atoms C.  $6.006 \div 1.008 = 5.958$ , or 6 atoms H.

The values do not always equal whole numbers because of errors in the experimental work. The molecular formula is  $C_6H_6$ .

Molecular equations. Reactions in which elementary gases are used should always be written to show the molecular formula of the element. If this is done the calculation of quantities can be very much simplified by making use of Avogadro's hypothesis.

Examples. The equation

$$2H_2+O_2\rightarrow 2H_2O$$

shows that two molecules of hydrogen combine with one molecule of oxygen. If 10 liters of hydrogen are used, it is clear that 5 liters of oxygen will be required to complete the reaction. Gases are usually measured by volume, so the volume result is all that is necessary.

Propane is C<sub>3</sub>H<sub>8</sub>. It burns to water and carbon dioxide, as do all carbon and hydrogen compounds:

$$C_3H_8+5O_2\longrightarrow 3CO_2+4H_2O$$

Therefore, 10 liters of propane would require 50 liters of oxygen for its combustion.

Ethyl alcohol is C<sub>2</sub>H<sub>5</sub>OH. Its combustion is thus shown:

Ten liters of alcohol vapor would require 30 liters of oxygen.

Ethane is C<sub>2</sub>H<sub>6</sub>. In writing the equation for its combustion, we first get

$$C_2H_6+O_2\rightarrow 2CO_2+3H_2O$$

We have seven oxygen atoms on the right side. The equation can only be balanced by taking the least common multiple of seven and two, the number of atoms in a molecule of oxygen. That will multiply  $O_2$  by seven and the other factors in the equation by two. We now have

$$2C_2H_6+7O_2\rightarrow 4CO_2+6H_2O$$

Ten liters of ethane would therefore require 10÷2×7, or 35 liters of oxygen.

#### **EXERCISES\***

- 1. Define equivalent weight.
- 2. State Avogadro's hypothesis.

<sup>\*</sup>Prepare this set of Exercises and hold it until those for Lessons XVII, XVIII, XIX, and XX are also prepared, and then send all five sets to the School.

- 3. State Gay-Lussac's law for combining volumes.
- 4. Show that oxygen contains two atoms per molecule.
- 5. Show that chlorine contains two atoms per molecule.
- 6. Show that the formula for water should be taken as H<sub>2</sub>O.
- 7. Define gram-molecular volume. What is its value?
- 8. Solve problem 1, page 289.
- 9. Solve problems 2 and 3, page 289.
- 10. Find the molecular formulas of the compounds from the following data:
  - (a) mol. wt. = 46, % C = 52.17, % H = 13.04, % O = 34.78
  - (b) mol. wt. = 58, % C = 82.76, % H = 17.24
  - (c) mol. wt. = 60, % C = 40.00, % H = 6.67, % O = 53.33
- 11. What volume of the first substance in the equations below will combine exactly with 50 liters of the second? Balance the equations:  $O_2+CH_3OH\rightarrow CO_2+H_2O$ ,  $P_4+Cl_2\rightarrow PCl_5$ ,  $HCN+O_2\rightarrow H_2O+CO_2+N_2$ ,  $H_2S+O_2\rightarrow SO_2+H_2O$ ,  $C_6H_6+O_2\rightarrow CO_2+H_2O$ ,  $H_g+O_3\rightarrow H_gO$ 
  - 12. Solve problems 4, 5, 7, 8, 10, and 11, pages 289 and 290.
- 13. When ozone acts, it first forms a molecule of oxygen and an atom of nascent oxygen. Assuming that 1 liter of ozone oxidizes some substance, not acted upon by molecular oxygen, to form a product not a gas, what volume of gas is left after the action?

### LESSON XVII

## COMPOUNDS OF CARBON

# Assignment: Chapters XXIV and XXV and Review of Chapter X. McPherson and Henderson

Organic Chemistry. Prior to 1827 chemists believed that chemical compounds belonged to two distinct classes. One class included all compounds that were formed in living bodies. Matter in the bodies of plants and animals is organized into cells and tissues, each of which has its function to perform in the life of the plant or animal. Because of this organization of matter, the compounds found in plants and animals or derived from them were called *organic compounds*.

The other class included the compounds found in the non-living, or mineral, world. The matter in these substances is not organized, and they are called *inorganic compounds*. It was believed that some kind of vital force was necessary to make the organic compounds, that they could not be made except in the living body. This belief is known now to be unfounded.

In 1827 Wohler made urea, a typical organic compound, from ammonium cyanate, a compound which can be made from the inorganic elements, carbon, hydrogen, oxygen, and nitrogen. Since then thousands of organic compounds have been made in factories and laboratories.

It is still customary, for convenience, to retain the names "organic" and "inorganic" as divisions of chemistry, though there is no fundamental distinction between them. Organic chemistry must, however, be given a different definition. It may be defined as the chemistry of the compounds of carbon. Some carbon compounds, like the oxides and the carbonates, are more like inorganic substances and are studied best in connection with other inorganic substances. With this in view, we call organic chemistry the study of the compounds of carbon and hydrogen and their derivatives. In an elementary course only a few of the many organic compounds can be mentioned.

Carbon monoxide. Carbon and carbon dioxide (CO<sub>2</sub>) have been studied in Lesson VI. Carbon monoxide (CO) is another oxide of carbon. It is found in volcanic gases; it may be prepared by reducing carbon dioxide:

## $CO_2 + C \rightarrow 2CO$

This occurs in hard-coal stoves. The blue flame observed at times is due to the burning of carbon monoxide above the hot coals. The decomposition of formic acid (HCHO<sub>2</sub>) or oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is used for its laboratory preparation (pages 292 and 293).

It is an odorless gas and an active poison. Deaths frequently result from the partial combustion of carbon compounds, as the incomplete burning of gasoline in a closed garage. Carbon monoxide is a good reducing agent because of its tendency to combine with oxygen. It is the real reducing agent in converting iron oxide to iron in the blast furnace. Mixed with hydrogen, it constitutes water gas, which is used for fuel.

Carbonates. Carbon dioxide is the acid anhydride of carbonic acid (H<sub>2</sub>CO<sub>3</sub>). When carbon dioxide is passed into water, the solution has the properties of a weak acid. It will neutralize bases to form salts, known as carbonates. The acid itself is so very unstable that it cannot be isolated. The reaction of water

and carbon dioxide is a reversible one, equilibrium being reached when only a small amount of carbonic acid is formed.

The salts of this acid are quite common. Limestone, shells, and marble are calcium carbonate (CaCO<sub>3</sub>). Washing soda is sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and baking soda is sodium acid carbonate (NaHCO<sub>3</sub>). The carbonates, except those of the alkali metals, are insoluble in water. They are acted upon easily by acids to liberate carbon dioxide. Calcium carbonate will dissolve in a solution of carbonic acid to form calcium acid carbonate (Ca(HCO<sub>3</sub>)<sub>2</sub>).

This happens in the formation of some kinds of hard water, when the water passes over limestone deposits. The acid carbonate can be decomposed by heating and the water softened in this way.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

Cyanogen and hydrocyanic acid. Carbon and nitrogen unite at high temperatures to form cyanogen  $(C_2N_2)$ . This is a very poisonous gas. Hydrogen, carbon, and nitrogen form a compound called hydrogen cyanide, or hydrocyanic acid (HCN). This is frequently called prussic acid, because of its relation to prussian blue  $(Fe_4(Fe(CN)_6)_3)$ . It is a weak acid. Both the acid and its salts are very poisonous. Compounds which can form the cyanide ion  $(CN^-)$  are very poisonous, while those that contain the cyanogen radical as a part of some more complex ion are not. The acid and its salts are used as bug poisons. Solutions of sodium and potassium cyanide are used in electroplating and to dissolve gold and silver in extracting these metals from their ores.

Hydrocarbons. Compounds of carbon and hydrogen are called hydrocarbons. These compounds are divided into two classes called aliphatic and aromatic. The paraffin, or methane, series is the principal series of the aliphatic hydrocarbons. The term "aliphatic" is taken from the fact that some of the higher members of the series are related to the common fats. The smaller-molecular-weight members of the methane series are given on page 297. Compounds of the same elements differing in composition by a common difference, or common group of atoms, as CH<sub>2</sub> in this case, are said to form an homologous series.

Acetylene (C<sub>2</sub>H<sub>2</sub>) is the first member of another homologous series. It has less hydrogen per carbon atom and is said to be unsaturated. The aromatic hydrocarbons take this name because most of the first known compounds in this class had a pleasant odor. The benzene series is the most important of this class. Benzene (C<sub>6</sub>H<sub>6</sub>) and toluene (C<sub>7</sub>H<sub>8</sub>) are its simplest and most common members. They are both obtained from coal tar and coal gas.

Petroleum. Rock oil, mineral oil, or petroleum, is chiefly composed of paraffin hydrocarbons and is the principal source of them. The crude oil may be used as a fuel, but it is usually refined by distillation. Fractions between different boiling points are taken. In the early days it was desirable to get as much kerosene (150° to 300°) as possible. Laws had to be passed requiring a product with a certain flash point. The temptation was to put into the kerosene too much of a lower-boiling fraction. If, on heating the oil, its vapor gave a flash of flame with a lighted match below a certain temperature, the oil was condemned as dangerous to use in lamps.

The temptation now is to put too much high-boiling fraction in the low-boiling fraction. Gasoline (70° to 150°) is now more in demand than kerosene. Commercial gasoline has as high a boiling point as can be used in the gasoline engine. To obtain from petroleum the maximum quantity of hydrocarbons which will boil low enough to form gasoline, the so-called cracking of oils is employed; this consists of vaporizing the oils and heating the vapor under considerable pressure. One of the methods is known as the Burton process. Under proper conditions, benzene and toluene are obtained by the process as well as low-boiling paraffins (pages 298, 299, and 300).

Methane (marsh gas). Methane (CH<sub>4</sub>) is called marsh gas because it is formed in marshes by decaying vegetable matter. It is also found in mines and therefore is likewise known as fire damp. It explodes with oxygen if ignited, the product being choke damp (CO<sub>2</sub>). To protect miners from dangerous explosions before mines were electrically lighted, Davy invented the miner's safety lamp (page 301). Methane is a constituent of coal gas and natural gas. It burns with a pale-blue flame, hence has no illuminating power. Methane is made in the laboratory by dis-

tilling a mixture of fused sodium acetate and sodium hydroxide. Sodium carbonate and methane are obtained:

Chloroform (CHCl<sub>3</sub>), iodoform (CHI<sub>3</sub>), and carbon tetrachloride (CCl<sub>4</sub>) are common halogen derivatives of methane.

Acetylene. Acetylene (C<sub>2</sub>H<sub>2</sub>) is made from calcium carbide and water:

$$CaC_2+2H_2O\rightarrow C_2H_2+Ca(OH)_2$$

The gas burns with a brilliant white light with plenty of air, but otherwise with a very smoky flame. It is used for lighting farm houses and was formerly much used in automobile lighting. It gives off much heat when burned and forms an intensely hot flame; for this reason it is used in the oxyacetylene blow-pipe for cutting and welding metal. It is also used to burn carbon out of the cylinders of gasoline engines.

Benzene. Benzene (C<sub>6</sub>H<sub>6</sub>) and toluene (C<sub>7</sub>H<sub>8</sub>) are obtained from the destructive distillation of coal (page 306)—some in the coal tar, more from the coal gas that distills over. Naphthalene (C<sub>10</sub>H<sub>8</sub>) and anthracene (C<sub>14</sub>H<sub>10</sub>) are obtained from the same source. Benzene is used as a fuel, as a solvent for fats, and in the manufacture of many useful substances such as dyes, perfumes, drugs, flavoring extracts, and explosives. Toluene has the same uses. T.N.T., a high explosive, is trinitrotoluene (C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>6</sub>). Naphthalene is used in moth balls and in making indigo. Anthracene is used to make alizarin, a red dye. Phenol, or carbolic acid, (C<sub>6</sub>H<sub>5</sub>OH) is found in coal tar or can be made from benzene. It is a poison and a good disinfectant. Picric acid, an explosive, is made from it. Saccharin is prepared from toluene. It is five-hundred times as sweet as sugar, but has no food value; it is not digested. Other derivatives of benzene are mentioned on page 337.

Fuels. Wood was doubtless the earliest fuel, and still is an important fuel where it is plentiful enough. Coal, in its different forms, is the most widely used fuel, but oils and gases are much used also. The navy has oil-burning ships, and some railroads in Texas and California use oil-burning engines. Gas was first used for lighting but now is used largely for fuel as well. There are several kinds of fuel gas. Acetylene has already been mentioned.

Others are coal gas, water gas, producer gas, and natural gas. A table showing the percentage composition of each is found on page 311.

Coal gas. The destructive distillation of coal has been referred to when discussing ammonia, coke, and coal tar. Coal was first distilled to get coal gas for illumination, the manufacture of which is described on pages 306 and 307. The coke made in this process is not enough to supply the demand. Much coke is made in the bee-hive ovens and in by-product ovens. The former oven is very wasteful, as the ammonia, coal tar, and coal gas escape, and it is being rapidly replaced by the by-product coke oven. These methods are described on page 308. Coal gas burns with a luminous flame because of the small amount of acetylene (C<sub>2</sub>H<sub>2</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) which it contains. These gases themselves burn with a smoky flame.

Water gas. Water gas is made by passing superheated steam over hot anthracite or coke, carbon monoxide and hydrogen being formed (page 308). It is very poisonous, because of the presence of carbon monoxide. It has no odor and burns with a non-luminous flame; to be used for lighting with an open jet burner, it must be enriched with hydrocarbons which will burn with a smoky flame. Water gas is enriched with petroleum products by passing the gas over hot fire bricks upon which the petroleum is sprayed. This cracks the petroleum, forming methane, acetylene, and ethylene among other products. Coal gas is sometimes enriched in a similar way.

Other gases. Producer gas is largely carbon monoxide. It can be made from a low grade of coal (page 310). It is used to run gas engines and in many metallurgical furnaces. Natural gas consists largely of methane; it has moderate luminosity and is used as a fuel as well as for lighting (page 310).

Flames. A flame is the result of the chemical union of two gases giving heat enough to produce light. The terms "combustible" and "supporter of combustion" are relative. We usually say that illuminating gas burns in air. Fig. 119, page 311, shows how air may be made to burn in an atmosphere of illuminating gas. If one of the substances taking part in the action is not a gas, no flame results, though light may be given off. Charcoal burns without a flame. Liquids and solids, like oil and wood, which

seem to burn with a flame, do so because the heat of the action vaporizes them or decomposes them into volatile substances (see the illustration with a candle flame, page 314). Note the discussion of oxidizing and reducing flames, page 318.

Luminosity of flames. The luminosity of a flame is due to the presence of some solid matter which becomes heated to a temperature sufficient to give off light. A difference in density of the gas in different parts of the flame, caused by decompositions, makes the gas visible. In ordinary flames, produced by burning carbon compounds, the luminosity is caused by particles of unburned carbon heated to high temperature. The carbon is formed by the partial combustion of the gas:

$$2C_2H_2+O_2\rightarrow 4C+2H_2O$$

The gas mantle employs the same principle. The mantle is composed of thorium and cerium oxides which are stable at high temperatures. A non-luminous flame is used to heat the mantle to a temperature where it gives off a brilliant white light (page 312).

Products of combustion of fuels. When fuels are completely burned, the products are carbon dioxide and water. These substances are not harmful, but burning fuels in rooms without ventilation soon uses up the oxygen necessary for respiration. If combustion is incomplete, harmful substances like carbon monoxide may form. Complete combustion forms no smoke. Smoke consists of carbon in a finely divided state, formed from the decomposition of the gases first formed from the fuel. To prevent smoke requires complete combustion of the fuels. Devices for this purpose provide a sufficient supply of air, thorough mixing of combustible gases with the air, and a temperature high enough to maintain combustion. (See the illustration on page 318.) Various fuels differ in their heat-producing, or calorific, value. The values for different fuels given on page 320 are obtained by the use of a bomb calorimeter (page 321).

#### **EXERCISES**

- 1. What is organic chemistry?
- 2. Give the methods for preparing carbon monoxide.
- 3. State the properties of carbon monoxide.
- 4. State the properties of carbonic acid.

- 5. What is prussic acid? Give its properties.
- 6. What are hydrocarbons? Name three series with examples of each.
- 7. What is meant by an homologous series? Illustrate.
- 8. Discuss the refining of petroleum.
- 9. Give the preparation and properties of methane.
- 10. Give the preparation and properties of acetylene.
- 11. Answer questions 2, 3, 4, 5, 6, 7, 8, 9, and 11, page 304.
- 12. Solve problems 12, 13, 14, 15, 16, 17, 18, and 19, pages 304 and 305.
- 13. Describe the manufacture of coal gas.
- 14. Describe the by-product coke oven.
- 15. How is water gas made?
- 16. How is producer gas made?
- 17. Discuss the composition, properties, and uses of the different fuel gases.
  - 18. What is a flame?
    - 19. State the cause of luminosity of a flame.
    - 20. Explain smoke prevention.
    - 21. What are meant by oxidizing and reducing flames?
    - 22. Answer questions 1, 2, 3, 5, 6, 8, and 10, pages 322 and 323.
    - 23. Solve problems 11 and 12, page 323.
- 24. What is meant by the "cracking of oil"? How and why is it carried out?

### LESSON XVIII

### COMPOUNDS OF CARBON—Continued

# Assignment: Chapters XXVI, XXVII, and XXXIII, McPherson and Henderson

Carbohydrates. We have seen that coal and petroleum are important sources of organic compounds. Another large source of organic compounds is the class of substances known as carbohydrates; they include the sugars, starch, cellulose, and such substances. The carbohydrates are commonly thought of as compounds of carbon, hydrogen, and oxygen, with the hydrogen and oxygen present in the proper proportions to form water. This definition of carbohydrates is not strictly correct (several exceptions are known), but it will serve our present purpose.

Carbohydrates may be divided into classes as: (1) single sugars, like dextrose and levulose, both of which have the formula,  $C_6H_{12}O_6$ ; (2) double sugars, like sucrose (common sugar), maltose (malt sugar), and lactose (milk sugar), all having the same molecular formula,  $C_{12}H_{22}O_{11}$ ; (3) more complex substances, like

starch and cellulose, both of which have a formula of  $C_6H_{10}O_5$  representing their percentage composition, but whose molecular weights are unknown. Substances like the sugars, which have the same molecular weight but different properties, are called isomeric. The difference in properties is due to a different arrangement of the atoms in the molecules.

Sucrose. This sugar is common sugar, familiar in granulated form. It is obtained from sugar cane and sugar beet chiefly. Maple sugar is a variety of sucrose, mostly desired for the impurities that flavor it. The sugar from cane and from the beet are the same chemical substance (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), except for small traces of impurities due to their different sources. These impurities are too small in amount to affect their properties materially, though they may cause slight differences in some respects. Popular opinion to the contrary notwithstanding, it has been shown that sugar from the beet will make good jelly, and pound for pound it is as sweet. The manufacture of sugar is discussed on page 325.

Sucrose does not ferment, but it can be split up into two single sugars, dextrose and levulose, by adding a molecule of water:

$$C_{12}H_{22}O_{11}+H_2O\rightarrow C_6H_{12}O_6+C_6H_{12}O_6$$

This reaction can be caused by heating the sucrose with a little dilute acid, or by the action of certain bacteria. This mixture is called *invert sugar*. Sucrose is decomposed by heat; a substance known as caramel is first formed, but the final product is carbon.

Lactose and maltose. Lactose is the sugar found in milk. It is added to cow's milk to modify the milk for feeding babies, as mother's milk contains a larger percentage of lactose than cow's milk. The sugar is added for its food value and not for the sweet taste; lactose is not very sweet, and for that reason is preferred to sucrose, though both have the same food value. When milk sours, lactose undergoes a change caused by bacteria; pasteurizing milk kills these bacteria and so keeps the milk sweet. When milk sours, lactic acid is formed.

Maltose is obtained by the hydrolysis of starch. Heating starch with a dilute acid, or the action of certain bacteria, first forms a substance known as dextrin, then maltose. The maltose then splits up into two molecules of dextrose. Maltose is formed in the process of making fermented liquors. It is also prepared in a form mixed with dextrin, which is used instead of lactose to modify milk for babies.

Dextrose. This is found in the juices of fruits and in honey together with levulose. It is especially plentiful in grapes and is called grape sugar. Commercially it is made from starch by heating it with hydrochloric acid. First the starch molecule is split up into dextrine, and then this into maltose, which in turn splits into dextrose. Most of the commercial product is a mixture of dextrose, maltose, and dextrin; it is known as glucose. Dextrose is a good food product but it is not so sweet as sucrose.

Starch. Starch is found in the seeds and roots of many plants; wheat, corn, barley, rice, and potatoes are common sources of it. The preparation of starch is described on page 327. Starch from different sources has a different appearance in the shape and size of the grains, so the source can usually be detected by the use of the microscope (see the illustrations on page 329).

Cellulose. This substance is the wood fiber of plants; cotton and linen are nearly pure cellulose. It is insoluble in most reagents but will dissolve in a solution of copper oxide in ammonium hydroxide. Boiling it with hydrochloric acid forms dextrose. Concentrated nitric acid converts it into cellulose nitrates, or nitrocellulose, commonly called guncotton, which has many commercial uses; photographic films, collodion, and celluloid are made from guncotton. Mercerized cotton and artificial silk are forms of cellulose (page 329). Paper consists mainly of cellulose. Cotton rags, linen, and wood pulp are used in making the different grades of paper. The method of manufacture is described on page 330.

Alcohols. Alcohols are a class of organic compounds which may be defined as hydroxides of the hydrocarbon radicals. They are the simplest oxidation products of the hydrocarbons, though they are not made from the hydrocarbons. They are usually obtained from natural sources. Three important alcohols may be considered here; they are methyl (CH<sub>3</sub>OH), ethyl (C<sub>2</sub>H<sub>5</sub>OH), and

glyceryl (C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>). The latter is the common substance known as glycerin. It is related to the hydrocarbon propane, three hydrogen atoms being replaced by three hydroxyl groups.

Methyl alcohol. This alcohol is commonly called wood alcohol. It is one of the products of the destructive distillation of wood. It has a lower boiling point than common alcohol and is very poisonous. It is used as a solvent and as a fuel. When its vapor, mixed with air, is passed over hot copper, oxidation takes place with the formation of formaldehyde (CH<sub>2</sub>O). This substance is a gas. A solution of it is commonly used as a preservative and disinfectant.

Ethyl alcohol. The common name of ethyl alcohol is grain alcohol. It is made by the fermentation of sugars, dextrose chiefly, by the action of common yeast (page 333). If starch is used in its preparation, it is first converted to dextrose, which ferments. Ethyl alcohol is intoxicating and in large amounts is a poison; it burns; it is used as a fuel, as a solvent, and in the preparation of other organic compounds. Ether, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, is made from it by the action of concentrated sulfuric acid; ether is used as an anesthetic in surgical operations.

For many purposes the alcohol is just as useful if rendered unfit for drinking by introducing into it bad smelling and tasting or poisonous substances. Methyl alcohol, benzine, and pyridine are used for this purpose. This product is called *denatured alcohol* and is free from the heavy government tax. In bread making alcohol and carbon dioxide are formed by fermentation caused by the yeast used. The carbon dioxide gas expands and escapes through the dough, making it light; on baking, the alcohol escapes also.

Glycerin. This alcohol is a by-product of the manufacture of soap. It is studied with soap in Chapter XXXIII, page 416. Alcohols are not bases but they do react with acids to form water and compounds like salts; these compounds are not salts and are called *esters*. The common fats are esters of glycerin and certain organic acids of large molecular weight. Both animal fats and vegetable oils belong to this class of compounds. When the fats are hydrolyzed by boiling with dilute acid or alkali they form glycerin and the acid or its alkali salt.

$$C_3H_5(C_{18}H_{36}O_2)_3+3NaOH\rightarrow C_3H_5(OH)_3+3NaC_{18}H_{36}O_2$$
  
fat glycerin soap

The above reaction is typical of what takes place in the formation of glycerin and soap. Glycerin is an oily liquid with a sweet taste. Its principal use is to prepare glyceryl nitrate, or nitroglycerin. It is also used in medicine.

Explosives. A rapid chemical action forming gases from liquids or solids causes an explosion because of the great volume change, the greater the volume changed the greater the explosion. Many explosives are organic compounds: the nitroglycerin above referred to is one; nitrocellulose is another; trinitrotoluene and picric acid are others (pages 420 and 421). These substances are used in making the smokeless powders. Dynamite is nitroglycerine absorbed in wood pulp with sodium nitrate added. Trinitrotoluene (T.N.T.) is a high explosive much used in the late war. Old-fashioned black gunpowder is a mechanical mixture of carbon, potassium nitrate, and sulfur, dry, finely ground, and in proper proportions to complete the equation

### $2KNO_3+3C+S\rightarrow K_2S+3CO_2+N_2$

Organic acids. The organic acids are oxidation products of the alcohols and are related to the hydrocarbons in a similar way. The most common series is known as the fatty-acid series because several of the higher members are fatty substances. The fatty-acid series is related to the paraffin hydrocarbons as follows: Methane (CH<sub>4</sub>), formic acid (HCHO<sub>2</sub>); ethane (C<sub>2</sub>H<sub>6</sub>), acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>). The common fats are esters of palmitic and stearic acids of this series and of oleic acid of another series. The glyceryl ester of butyric acid is the constituent of butter that distinguishes it from other fats. These acids are monobasic and weak.

Acetic acid. This acid was one of the earliest acids known. It is the sour constituent in vinegar. Commercially, it is obtained as a product of the destructive distillation of wood (page 120). Acetic acid forms many salts with the metals, as well as esters with the alcohols. Lead acetate ( $Pb(C_2H_3O_2)_2$ ), known as sugar of lead, is used in sugar analysis. Sodium acetate ( $NaC_2H_3O_2$ ) is another. Ethyl acetate ( $C_2H_5C_2H_3O_2$ ) is an example of an ester of the acid. Vinegar is a dilute solution of acetic acid, together

with certain flavoring substances derived from the fruit juices from which it is obtained. In making eider vinegar, the sugar of the apple juice is first fermented to alcohol by yeast and then oxidized to acetic acid by the bacteria found in "mother of vinegar." Distilled vinegar is simply dilute acetic acid made from pure dilute alcohol. It leaves no solids on evaporation. Other vinegars do, and an analysis of these solids will show the source of the vinegar.

Fats. The common fats and oils are esters of oleic, palmitic, and stearic acids with glycerin. These esters are called olein, palmitin, and stearin. They have different melting points. The various fats are mixtures of these three in different proportions. Olive oil and cottonseed oil are largely olein. Lard contains more palmitin and stearin. Tallow is largely stearin. Butter is mostly composed of these fats, but its characteristic flavor is due to butyrin. Butyrin is more readily hydrolyzed than the other fats, forming glycerin and butyric acid. This causes the butter to become rancid in taste and smell. Oleomargarine has the same composition except for the butyrin; it will not become rancid as soon as butter. It equals butter in food value but lacks its flavor. In butter there are also what are known as vitamines, or substances containing "the growth principle." These substances are found in milk, green vegetables, and near the surface of seeds. Lard substitutes can be made from oils, as cottonseed oil, by adding hydrogen. Olein is thus converted into stearin.

Foods. Food is classified into fats, carbohydrates, proteins, mineral matter, and water. Vitamines may be added to this list. Fats and carbohydrates have been discussed. They are composed of carbon, hydrogen, and oxygen. Proteins are substances containing nitrogen in addition to the above elements. Albumin, casein, and the gluten of wheat are protein-containing substances; lean meat and dried beans are also rich in protein. Protein is the essential substance in building up the tissues of the body. Fats and carbohydrates are oxidized to furnish the heat of the body. Observe the composition of various foods as given on page 344.

Soap. Soap is either a sodium or a potassium salt of the acids whose esters are found in the common fats; sodium forms a

hard soap and potassium a soft soap. The fats or the vegetable oils are treated with sodium or potassium hydroxide. Usually the substances are heated together, but there is a cold process. The reaction is the same as for the preparation of glycerin. The commercial process is described on page 417. Soap is soluble in water and reacts slightly with it, giving an alkaline reaction. Calcium and magnesium compounds form insoluble precipitates with soap. Water containing salts of these metals is known as hard water, as they do not lather with soap. Soap cleans largely because of its ability to form an emulsion (page 387).

#### **EXERCISES**

- 1. What are carbohydrates?
- 2. Classify carbohydrates. Give examples of each class.
- 3. What are isomeric substances? Give an example.
- 4. How is sucrose made? What are its sources?
- 5. State the chemical behavior of sucrose.
- 6. State the source and properties of lactose.
- 7. What is the source of maltose?
- 8. How is dextrose made? What are its natural sources?
- 9. Describe the manufacture of starch.
- 10. What is cellulose? What important substances are made from it? Give their uses.
  - 11. How is paper made?
  - 12. What are alcohols?
  - 13. Give the name and the formula for three alcohols.
  - 14. State the preparation and the properties of wood alcohol.
  - 15. Give the preparation and the properties of grain alcohol.
  - 16. What is denatured alcohol?
  - 17. How is glycerin made? Give its uses.
  - 18. Give the preparation of the common explosives.
  - 19. What are the fatty acids? Give two examples.
  - 20. Describe the preparation of acetic acid. What are its properties?
  - 21. How is vinegar made? How does cider vinegar differ from acetic acid?
- 22. What are the fats? Give examples. What is butter? What is oleomargarine?
  - 23. Give the classes of foods and examples of each class.
  - 24. How is soap made?
  - 25. Explain the cleansing action of soap. What causes hard water?
  - 26. Answer questions 5, 7, 8, and 9, page 338.
  - 27. Answer questions 6, 8, 9, 10, and 11, page 422.
  - 28. Solve problems 10, 11, 13, 14, and 15, page 338.

### LESSON XIX

# THE PHOSPHORUS FAMILY; SILICON AND BORON THE PHOSPHORUS FAMILY

Assignment: Chapter XXVIII, McPherson and Henderson

The phosphorus family. The phosphorus family includes nitrogen as well as the elements listed at the top of page 346. Their properties vary with increasing atomic weight, as in the chlorine family. Here, however, chemical activity is not so great and it is not to our advantage to compare them in that respect. More can be learned about their properties by comparing their tendency to increase in metallic properties as atomic weights increase. All the elements of this family form two series of compounds. In one they have a valence of three, in the other, five. The element is more positive, or metallic, in properties when acting in its trivalent form. A consideration of each element in these two respects will be worth while.

Nitrogen is decidedly a non-metal. It is sometimes positive as in the oxides, but its oxides which are anhydrides form acids. The trivalent one, nitrous acid, is rather weak, but still distinctly an acid. The acid of pentavalent nitrogen, nitric acid, is a very strong acid, showing that the high-valent form is more negative and a better acid former. Nitrogen halides are very unstable as nitrogen has little tendency to combine positively.

Phosphorus, with the next higher atomic weight, is a solid, has a waxy luster, but is non-metallic in physical properties. In chemical action it is sometimes positive, as in combination with oxygen and the halogens. These compounds are more stable than the corresponding ones for nitrogen. Phosphorus forms no salts with the acids. Its oxides are always acid-forming and never base-forming anhydrides. Its acids are both weak, but phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), derived from the pentoxide (P<sub>2</sub>O<sub>5</sub>), is the stronger.

Arsenic shows more positive properties and weaker negative properties. It is, however, still strongly negative, that is, non-metallic in behavior. It is a black solid, with dull metallic luster. Its oxides are anhydrides of weak acids, of which the one con-

taining pentavalent arsenic is the stronger. Arsenic forms a sulfide which can be precipitated as metallic sulfides are precipitated.

Antimony has a bright metallic luster and appears like a metal. Its trioxide (Sb<sub>2</sub>O<sub>3</sub>) is equally a basic and an acid anhydride. The trioxide is insoluble in water, but will dissolve equally well in hydrochloric acid, forming a chloride (SbCl<sub>3</sub>), or in sodium hydroxide, forming a sodium salt (Na<sub>3</sub>SbO<sub>3</sub>). The hydroxide (Sb(OH)<sub>3</sub>) is equally an acid and a base. Several other metallic hydroxides have acid properties as well as basic properties, such as those of aluminium, zinc, and lead. Such hydroxides are called amphoteric hydroxides (page 361). Antimony exhibits its more metallic properties by forming a sulfate. It does not form a nitrate.

Bismuth is decidedly a metal. It not only has metallic luster and the other physical properties of a metal, but it acts chemically like a metal. All the other elements of the family form compounds with hydrogen; bismuth does not. Its oxides are but slightly acid forming. The trioxide is predominately a basic oxide; it reacts with all the common acids to form salts. Bismuth nitrate, carbonate, and phosphate are easily formed salts; such salts are not known for other members of the family.

Phosphorus. One of the principal sources of phosphorus is the bones of animals, where it occurs as calcium phosphate. Calcium phosphate also occurs as a mineral in the form of phosphorite. Phosphorus is a very active element with oxygen and for that reason does not occur free in nature. Phosphorus is a necessary constituent of plants and must occur in fertile soils in soluble form; calcium phosphate is used in the manufacture of fertilizers. Phosphorus is made from bone ash or phosphate rock by heating with silica (SiO<sub>2</sub>) and carbon in an electric furnace (page 348).

The element is known in several allotropic forms, of which the white or yellow is the common form. The red form is used for many purposes. The two forms differ in properties. The first is poisonous, easily ignites, and is soluble in carbon disulfide. The second is not poisonous, does not ignite so easily, and is not soluble in carbon disulfide. Yellow phosphorus combines slowly with oxygen at ordinary temperatures giving a pale light in the

dark. It is liable to spontaneous combustion. The change from yellow to red phosphorus is a reversible action (page 349).

Uses of phosphorus. Yellow phosphorus is used as a poison for rats. Both forms are used in chemical work. The chief use of the element is in the preparation of matches. Matches were formerly made from yellow phosphorus, but on account of its poisonous effect on the workers, its use is either prohibited or taxed out of existence. Instead, a sulfide (P<sub>4</sub>S<sub>3</sub>) is used. With this an ordinary oxidizing agent and a binding material are used. Safety matches are red phosphorus and an oxidizing agent on the box and antimony sulfide and an oxidizing agent on the match tip (page 350).

Acids of phosphorus. The two oxides of phosphorus are the trioxide  $(P_2O_3)$  and the pentoxide  $(P_2O_5)$ ; both form acids of phosphorus in combination with water:

The last is the most important, and its salts are the common phosphates. It is usually called phosphoric acid without the prefix. It is formed when the pentoxide reacts with hot water; with cold water, the pentoxide forms metaphosphoric acid. Pyrophosphoric acid is formed from orthophosphoric acid by heating it to 225°. The salts of the phosphorous acids are not frequently met with.

Arsenic. This element occurs largely in the free state, as sulfides, and as the oxide (page 355). It is prepared by the reactions shown on pages 355 and 356. Its chief use is as an alloy with lead, used in making shot. Most of its compounds are poisonous, but the element is not. Nitric acid converts arsenic to arsenic acid. Hydrochloric acid has no action on it. With nascent hydrogen it forms arsine (AsH<sub>3</sub>). Marsh's test for arsenic consists of the preparation of arsine and a study of the properties by which it can be recognized (page 357). Very small amounts of arsenic can be detected by this method. Arsenic trioxide (As<sub>2</sub>O<sub>3</sub>)

is commonly called white arsenic. It is frequently given as a poison and is used in the manufacture of glass, dyes, and insecticides. The acids of arsenic and their salts are similar in composition and properties to those of phosphorus. Paris green is a copper salt of complex formula used as an insecticide. Lead arsenate is used to spray trees.

Antimony. The mineral stibnite (Sb<sub>2</sub>S<sub>3</sub>) is the source of antimony, which is prepared by heating the sulfide with iron (page 360). Nitric acid converts antimony to an insoluble oxide; aqua regia forms antimony chloride; hydrochloric acid does not act on it. It forms oxides and acids similar to those of phosphorus, but much weaker. Stibine (SbH<sub>3</sub>) is formed in Marsh's test, if antimony salts are present. The two elements give different reactions and can easily be distinguished (page 360). Antimony is used in alloys. Antimony salts react with water; but the hydrolysis is only a partial one. In antimony chloride only two of the chlorine ions are replaced by hydroxyl ions (page 362).

## SbCl<sub>3</sub>+2HOH→Sb(OH)<sub>2</sub>Cl+2HCl

This forms a *basic salt*, which, however, loses a molecule of water and becomes SbOCl; this is called antimony oxychloride.

Bismuth. Bismuth is usually found in the free state and is prepared by melting the ore and allowing the liquid to run into vessels (page 363). Bismuth forms the nitrate with nitric acid and the sulfate with hot concentrated sulfuric acid, but hydrochloric acid does not act with it. Its principal oxide is the trioxide (Bi<sub>2</sub>O<sub>3</sub>), which is mostly basic in its properties. Bismuth salts hydrolyze partially like those of antimony. Bismuth oxynitrate (BiONO<sub>3</sub>), called bismuth subnitrate, is used as a medicine in certain kinds of stomach trouble. Bismuth is used in alloys.

Alloys. Alloys are substances formed by melting metals together. While liquid, a solution is formed. On cooling we have what is called a solid solution. Most alloys are of this kind. Some are known to be definite compounds of the metals with each other. Lead and copper are metals much used in making a great variety of alloys. The many varieties of steel are formed by making iron alloys with different metals and with carbon.

The melting point of most alloys is below the average melting point of the constituents and in many cases below that of any of them.

Antimony alloys expand on solidifying and for that reason are suitable for making type. Type metal consists of antimony, tin, and lead. Babbitt metal contains the same elements with a little copper added. Bismuth alloys have a very low melting point; some of them melting below the boiling point of water. Wood's metal, which consists of bismuth, lead, tin, and cadmium, melts at about 60°. These alloys are used in automatic fire-extinguishing apparatus (page 365). Brass is an alloy of copper and zinc. Other copper alloys are listed on page 497. Alloy steels and their uses are given on page 481. Nickel, tin, zinc, and aluminium are also used in different alloys. Solder is an alloy of lead and tin. Coin metals are alloys of copper, nickel, silver, and gold.

### SILICON AND BORON

## Assignment: Chapter XXIX, McPherson and Henderson

Silicon. This element belongs in Periodic Group IV with carbon and resembles carbon in some respects. The valence of silicon is four, and in the silicates we find a large number of complex compounds. As silicon dioxide (SiO2) or silicates of the metals it is a constituent of a large part of the substances which make up the crust of the earth, such as granite, sandstone, clay, and shale. Silicon is made by reducing silicon dioxide with aluminium or carbon. It is used in the metallurgy of iron as ferrosilicon. Silicon forms silicides with several elements. Carborundum, or carbon silicide (CSi), is a very hard substance used as an abrasive in place of emery. For other properties of silicon see page 368. Carborundum is made in an electric furnace (page 370). Silicon dioxide occurs in nature in a great variety of forms, as quartz, sand, onyx, opal, flint, and agate. Infusorial earth is a form of silicon dioxide derived from the skeletons of certain microörganisms; it is used in making scouring soaps. Quartz is used to make dishes for laboratory use. Silicon dioxide is the anhydride of two acids, orthosilicic acid (H<sub>4</sub>SiO<sub>4</sub>) and metasilicic acid (H<sub>2</sub>SiO<sub>3</sub>); many of the simple silicates are salts

of the latter, as calcium metasilicate (CaSiO<sub>3</sub>); mica (KAlSiO<sub>4</sub>) is a salt of the former.

A large number of silicates are complex compounds containing the acid radical of what are called condensed silicic acids; that is, two or more molecules of silicic acid (H<sub>4</sub>SiO<sub>4</sub>) lose one or more molecules of water to form the condensed acid. Thus:

$$3H_4SiO_4\rightarrow H_4Si_3O_8+4H_2O$$

Feldspar (KAlSi<sub>3</sub>O<sub>8</sub>) is a salt of this acid. Pure clay, or kaolin, is Al<sub>2</sub>Si<sub>2</sub>O<sub>7.2</sub>H<sub>2</sub>O. Water glass is sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>). It is used to preserve eggs, in waterproofing porous materials, as a glue for glass and pottery, to make curtains non-inflammable, and in soaps (page 374).

Glass. Glass is a solid solution of different silicates and silicon dioxide. Common glass contains the silicates of sodium and calcium. In other glasses, potassium is substituted for sodium to give hardness and a higher melting point. Lead is used in place of calcium to give a low-melting glass. Lead and barium both give a high refractive index. Lead glass is used in making optical instruments. Glass is colored with various metallic oxides which fuse along with the glass; milky glass has tin oxide or some white infusible substance present. Enamels for surfacing metal vessels are a kind of opaque glass which contain the oxides of boron in place of some of the silicon dioxide, and oxides of zinc, lead, or barium in place of some of the calcium. A full description of the manufacture of glass is given on pages 374–377.

Boron. Boron occurs in the third periodic group. Other members of this group have metallic properties, but boron is a non-metallic element. Its oxide (B<sub>2</sub>O<sub>3</sub>) is an acid anhydride, forming boric acid (H<sub>3</sub>BO<sub>3</sub>). This acid occurs in nature. Another source of boron is borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>). This compound is a salt of tetraboric acid, a condensed acid of boric acid. Boric acid can be made from borax by treating it with sulfuric acid:

# Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>+5H<sub>2</sub>O+H<sub>2</sub>SO<sub>4</sub>→Na<sub>2</sub>SO<sub>4</sub>+4H<sub>3</sub>BO<sub>3</sub>

Borax is a hydrate with either five or ten molecules of water. It is used in making enamels and glazes. Borax fuses, loses its water, and forms a glass which will dissolve metallic oxides with characteristic colors in many cases. It is used in analysis to

detect these metals. Cobalt gives a deep blue, chromium a green, and iron a yellow color. Borax, being a salt of a weak acid and a strong base, has an alkaline action toward litmus. It is used to soften water, as an antiseptic, and in brazing.

### **EXERCISES**

- 1. Name the elements of the phosphorus family in order of increasing atomic weights.
- 2. Discuss the variation of their positive and negative properties as atomic weight increases.
- 3. Compare positive and negative properties of the two different valence forms.
- 4. Compare the properties of the yellow and the red forms of phosphorus.
  - 5. Give the composition of the different kinds of matches.
- 6. Write equations showing the relation of the oxides of phosphorus to the acids.
  - 7. Name the sources of calcium phosphate. What is its use?
- 8. State the action of arsenic, antimony, and bismuth with hydrochloric and nitric acids.
  - 9. Describe Marsh's test for arsenic.
  - 10. Give the uses of arsenic, antimony, and bismuth as elements.
  - 11. Explain the hydrolysis of bismuth nitrate.
  - 12. What are alloys? Name five alloys, their composition, and uses.
  - 13. What is silicon used for? Give its sources.
  - 14. What is carborundum? How is it made? What is its use?
  - 15. Name a number of sources of silicon dioxide. What are its uses?
- 16. Give names and formulas for the acids of silicon. Name a salt of each acid.
  - 17. What is water glass? How is it made? What are its uses?
  - 18. Describe the manufacture and the blowing of glass.
  - 19. What is glass? What are the varieties of glass? How is it colored?
  - 20. How is boric acid made? What is borax? Give its uses.
  - 21. Answer questions 2, 5, 6, 7, 9, 11, and 12, pages 365 and 366.
  - 22. Solve problems 8, 15, 16, and 17, page 366.
  - 23. Answer questions 2, 4, 5, 6, and 7, page 381.

## LESSON XX

## METALS; ALKALI FAMILY

### **METALS**

# Assignment: Chapter XXXI, McPherson and Henderson

The metals. The elements have already been referred to as acid forming and base forming. From the point of view of their chemical reactions, the metals may be defined as those elements which

can become cations of bases. As we saw in the study of antimony, the distinction between a metal and a non-metal is not a sharp one. This element and several others have both metallic and non-metallic properties. In most cases one or the other kind of property predominates. The metals are solids, except mercury, which is a liquid. Most of them have a high density, though the alkali metals are lighter than water. They are conductors of heat and electricity and have a high luster. Most of them combine readily with oxygen and other negative elements, their surfaces tarnishing if the action is not complete. The chemical properties of the metals are in accord with their position in the electrochemical series (page 191), a review of which at this time would be profitable.

Extraction of metals. Most of the metals are found in nature in combination, but gold and frequently silver and copper are found free. Minerals are inorganic substances found in nature. An ore is a mineral from which a useful substance can be extracted. The extraction of metals from their ores is called metallurgy.

Two methods of metallurgy are in use, reduction and electrolysis. Reduction may be accomplished with carbon, as in the case of iron, zinc, and tin, if the ore is an oxide. Many ores which are not oxides can be converted into oxides by roasting the ore; carbonates form oxides on heating; sulfides must be heated in a current of air. More refractory oxides are not reduced by carbon, and in such cases aluminium can be used as the reducing agent. Chromium and manganese are made this way.

If the ore is soluble or can be easily converted into a soluble compound or if it fuses readily, it can be decomposed by the electric current. The metal deposits at the cathode if it does not combine with the water present. Sodium, which would combine with water, is made by electrolysis of a fused compound. Electrolysis is used to refine some metals which are obtained in impure form by other methods.

Not all the electrochemical industries are electrolytic. Many of them use electric energy simply as a method of generating heat. Such are the preparation of carborundum, graphite, and carbon disulfide. Water power is essential for the generation of cheap electric energy. For this reason many of our electrochemical industries are located at Niagara Falls (illustration page 392).

Preparation of compounds of metals. Compounds of the metals are prepared by employing the same types of reaction which have already been studied. These are addition, or combination, of elements, decomposition of a compound, substitution of one element for another, and double decomposition. Double decomposition is most frequently carried out in solution.

It is necessary that the conditions be such as to permit the reactions to go to completion (page 224). This may happen in one of three ways: (1) an insoluble gas may be formed; (2) an insoluble solid may form; (3) an undissociated molecule may form. Reactions of these types can be employed in preparing metallic compounds if the proper materials are selected. Some substances are not soluble in water or acids and so cannot be brought into double decomposition in the usual way. Many such insoluble substances are soluble in melted sodium carbonate and can be brought into reaction by fusing with it. Since the carbonate formed by double decomposition is insoluble in the sodium carbonate, completion of the reaction is made possible.

We have, then, altogether, seven ways to make compounds of metals:

- 1. Combination, Zn+O→ZnO
- 2. Decomposition, CaCO<sub>3</sub>→CaO+CO<sub>2</sub>
- 3. Substitution, CuSO<sub>4</sub>+Zn→ZnSO<sub>4</sub>+Cu
- 4. An insoluble gas, CaCO₃+2HCl→CaCl₂+CO₂+H₂O
- 5. An insoluble solid, Pb(NO<sub>3</sub>)<sub>2</sub>+Na<sub>2</sub>SO<sub>4</sub>→PbSO<sub>4</sub>+2NaNO<sub>3</sub>
- 6. An undissociated molecule, Ca₃(PO₄)₂+6HCl→3CaCl₂+2H₃PO₄
- 7. Fusion, PbSO<sub>4</sub>+Na<sub>2</sub>CO<sub>3</sub>→PbCO<sub>3</sub>+Na<sub>2</sub>SO<sub>4</sub>

The preparation of zinc sulfate by using zinc and sulfuric acid, hydrogen gas being set free, is an example of method No. 3 and not of No. 4, which is a type of double decomposition first of all, while in preparing zinc sulfate, the element hydrogen is replaced by zinc (substitution). The example given under method No. 6 is that of an undissociated molecule because phosphoric acid is a very weak acid and is practically undissociated in the presence of the stronger hydrochloric acid.

Insoluble compounds. In order to apply methods 4 and 5 it is necessary to know what substances are insoluble. The solubility of gases varies somewhat with conditions, but we have found it possible to establish conditions whereby hydrochloric acid,

hydrogen sulfide, ammonia, carbon dioxide, and nitric acid are insoluble. They are all prepared according to method 4.

Insoluble solid compounds of the metals can be made by precipitation according to method 5. To carry out such a reaction, it is necessary to start with two water-soluble substances. One must contain the metal of the compound it is desired to prepare; the other, the negative radical. Then, when these solutions are brought together, the metal and negative radical will combine and precipitate out, if they form an insoluble compound. A table of the insoluble salts of the several acid radicals is given on pages 394 and 395. It should be studied carefully and frequently referred to.

### ALKALI METALS

# Assignment: Chapter XXXII and Review of Chapter XV, McPherson and Henderson

Characteristics of family. This family occurs in Group I of the periodic table. It consists of lithium, sodium, potassium, rubidium and caesium. Note the relation between their atomic weights and physical properties (page 396). As in the chlorine and phosphorus families, these metals show a marked gradation in properties as their atomic weight increases. They are the most positive family of elements, that is, the strongest metals. Their hydroxides are strong bases. As the atomic weight increases, their metallic properties become stronger. Potassium hydroxide is a stronger base than sodium hydroxide, and caesium hydroxide is the strongest of all bases. They occur at the top of the electrochemical series of the metals, showing their very positive properties.

Except as they vary in strength of chemical activity, they are very similar in properties. They always combine with a valence of one. All their important salts are soluble in water, and for this reason their compounds are frequently found in sea water or in salt beds formed by evaporation. Their activity with oxygen and water is so great that they must be kept under an oil, like kerosene. Of these elements, only sodium and potassium are common enough to demand special study. Sodium was studied in Lesson IX, which should be reviewed at this point.

Compounds of sodium. Sodium chloride (NaCl), common salt, is the chief source of sodium and sodium compounds. It is found in salt water and in salt beds in many localities. It is used as table salt and in the preparation of soap, glass, soda, bleaching powder, and hydrochloric acid. Most salt contains small amounts of calcium and magnesium chlorides and for that reason absorbs moisture. Shaker salt is kept dry by mixing with it a little finely powdered calcium phosphate.

Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) is formed in making hydrochloric acid and is used in making sodium carbonate. Its hydrate (Na<sub>2</sub>SO<sub>4</sub>.10H<sub>2</sub>O) is known as Glauber's salt. Sodium sulfate is used as a laxative in cattle powders. It is also used in making glass. Hypo is used by photographers to dissolve unchanged silver salts and is employed in bleaching to absorb excess chlorine. It has the formula Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, which is sodium thiosulfate.

Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) is made in two ways. The older method, known as the Leblanc process, was devised during the French Revolution (page 403). It is now largely replaced by the Solvay process, devised by a Belgian chemist. The reactions involved in these two processes are shown on page 402. It will be noticed that hydrochloric acid is a by-product of the Leblanc process. The sale of this enables the few Leblanc plants to continue to operate on a paying basis. Sodium carbonate forms a hydrate (Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O), which is known as washing soda or sal soda. It is used to soften water and in the manufacture of glass and soap. It hydrolyzes with an alkaline action. It is used in laundry work because the alkaline action cuts grease.

Sodium hydrogen carbonate (NaHCO<sub>3</sub>), commonly called bicarbonate of soda, is baking soda. It is made in the Solvay process or by passing carbon dioxide into a solution of sodium carbonate. It is used in baking and in making baking powder.

Sodium nitrate (NaNO<sub>3</sub>) is Chili saltpeter. It is used in making nitric and sulfuric acids and in the manufacture of fertilizers. This is the only nitrate found extensively in nature. The largest deposits are in Chili. Sodium cyanide (NaCN) is another important salt of sodium. It is used in gold mining because its solutions dissolve elementary gold. The compound is extremely poisonous. Sodium hypochlorite (NaClO) is an unstable

compound, obtained only in dilute solution. It is prepared by the reaction shown on page 406. It is used as a bleaching and antiseptic agent. Sodium compounds impart a yellow color to a colorless flame.

Potassium. Potassium compounds are abundant, but many of them are silicates and hence insoluble and very hard to decompose. For this reason it is so difficult to obtain the potassium in usable form that these compounds are not an important source of potassium. The common source of potassium salts is the large deposits of chloride and sulfate at Stassfurt, Germany (page 407). Potassium is a necessary element in plant foods, and it must occur in water-soluble compounds which can be absorbed by the roots of the plants. Plant ashes are a source of potassium carbonate.

Potassium salts are used in fertilizers, and during the war fertilizer manufacture was seriously handicapped by the lack of such salts, formerly imported from Germany. Other sources (page 408) of potassium salts were developed as much as possible but the supply could not nearly meet the demand. Potassium and potassium hydroxide are made exactly like sodium and sodium hydroxide (pages 173 and 176). Saltpeter, potassium nitrate (KNO<sub>3</sub>), is used in making gunpowder, as a preservative, and in medicine. It is a good oxidizing agent. It is now made from sodium nitrate, but formerly it was obtained from manure by the oxidizing action of bacteria on the organic compounds containing potassium and nitrogen. Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) can be made by the Leblanc process, but not by the Solvay process because potassium hydrogen carbonate is too soluble to be precipitated. Potassium compounds give a purple color to a colorless flame (page 414).

Ammonium compounds. The ammonium radical (NH<sub>4</sub>) has positive properties, forming a cation. The base (NH<sub>4</sub>OH) was studied in Lesson XII. Its salts are usually classified with the salts of the alkali metals. The radical is univalent, and the salts are generally soluble in water. Ammonium salts are found in the soil in small quantities, being formed by the decay of nitrogen containing organic matter. Commercially, they are obtained from the ammoniacal liquors produced in making coke (page 306). Ammonium chloride (NH<sub>4</sub>Cl), called sal ammoniac, is used in dry cells, in soldering, in medicine, and as a reagent.

colored fires.

#### **EXERCISES**

- 1. What is a metal, a mineral, an ore? Define metallurgy.
- 2. Name the methods for obtaining metals from ores. Illustrate.
- 3. What is roasting? How is it done and why?
- 4. Give the seven methods for making compounds of the metals. Write two equations to illustrate each.
- 5. State the solubility of chlorides, sulfates, carbonates, nitrates, and phosphates.
- 6. Answer questions 1, 2, 3, and 4, page 395. Assign each equation written to one of the seven methods for making compounds.
  - 7. Discuss the characteristics of the alkali metals.
- 8. Give chemical name, formula, and use for the following: caustic soda, washing soda, sal ammoniac, caustic potash, saltpeter, baking soda, borax, hypo, Glauber's salt, Chili saltpeter.
- 9. Describe, giving equations, the Leblanc and the Solvay processes for making sodium carbonate.
  - 10. How are potassium hydroxide and potassium carbonate made?
  - 11. Give the flame tests for sodium and potassium.
  - 12. Answer questions 2, 4, 5, 9, 11, and 18, pages 414 and 415.
  - 13. Solve problems 7, 8, and 13, page 415.

### SEND EXERCISES FOR LESSONS XVI-XX TO THE SCHOOL

## LESSON XXI

# THE CALCIUM AND MAGNESIUM FAMILIES CALCIUM FAMILY

# Assignment: Chapter XXXIV, McPherson and Henderson

Characteristics of family. The metals of this family are calcium, strontium, and barium—sometimes called the alkaline-earth metals. They form weaker bases than the metals of the alkali family. Many of their compounds are found in the earth's crust as carbonates and silicates. Calcium is by far the most abundant. None of them occurs free in nature as they are too active, though not so active as the alkali metals. They follow the alkali metals in the electrochemical series. They act slowly with water at ordinary temperatures, forming hydrogen. They burn brilliantly in oxygen or the air. With a colorless flame, calcium compounds give a yellowish-red, strontium a crimson, and barium a green color. Strontium and barium compounds are used in making

Compounds of calcium. Calcium oxide (CaO), commonly called lime, or quicklime, is obtained by heating calcium carbonate in the form of limestone or marble. It is used to make slaked lime by adding water. This forms calcium hydroxide (Ca(OH)<sub>2</sub>). Slaked lime is used extensively in building as a constituent of mortar and plaster. Quicklime absorbs carbon dioxide from the air as well as moisture, so air-slaked lime contains calcium carbonate. Lime is used as a soil dressing because it neutralizes the organic acids in sour soil, thus producing more favorable conditions for bacterial action to convert organic nitrogen into forms available for plant food.

Limewater is a solution of calcium hydroxide. It is used some in medicine. Calcium hydroxide is used in making ammonia and bleaching powder and to remove hair from hides. Mortar is a mixture of calcium hydroxide and sand; plaster contains hair in addition. Mortar hardens and sets because it absorbs carbon dioxide from the air to form calcium carbonate (page 427).

Bleaching powder is made by passing chlorine over lime. The compound formed is a double salt containing two acid radicals (CaClOCl), being a salt of hydrochloric (HCl) and hypochlorous (HOCl) acids. It is sometimes called chloride of lime. It is used for bleaching, and as a disinfectant because of the chlorine liberated. It is used to purify city water.

Calcium carbonate occurs in nature in a variety of forms, as limestone, marble, pearls, coral, shells, and chalk (page 428). It is largely used as a building stone and in the manufacture of glass, cement, soda, lime, and carbon dioxide. Pure calcium carbonate is precipitated from solutions of sodium carbonate and calcium chloride. This is called precipitated chalk and is used in making tooth powder.

Calcium sulfate occurs in nature in the form of gypsum, which has the formula CaSO<sub>4</sub>.2H<sub>2</sub>O. Gypsum is used in making paper and plaster of Paris. When gypsum is heated to about 125° C., it loses three-fourths of its water, forming plaster of Paris (CaSO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O. This compound absorbs water and hardens by again forming gypsum. It is used to make plaster casts for broken bones, in stucco work, and as a finishing coat in plastering walls.

Calcium carbide is made by heating lime and carbon in an electric furnace (page 432). It is used in making acetylene, and nitrogen passed over hot calcium carbide forms calcium cyanamide (page 433). This latter compound (CaCN<sub>2</sub>) is a useful fertilizer its value depending upon its reaction with water to form ammonia This is one of the methods of converting atmospheric nitrogen into compounds of nitrogen.

Hard waters and boiler scale. Hard water is caused by compounds of calcium and magnesium in solution. Temporary hardness can be removed by boiling, permanent hardness cannot Temporary hardness is caused by the presence of acid carbonates of calcium and magnesium. When water, containing carbon dioxide, passes over limestone, the acid dissolves the carbonate, forming calcium acid carbonate (Ca(HCO<sub>3</sub>)<sub>2</sub>). This is soluble, but is unstable when heated, and boiling the water decomposes it, forming calcium carbonate. Calcium hydroxide is used sometimes to neutralize the acid carbonate. (See the equations on page 431.) Magnesium compounds behave in a similar way.

Sulfates and chlorides of these metals are dissolved by water As these compounds are stable and are not removed by boiling such hardness is called permanent. The water is softened by precipitating the carbonates with sodium carbonate (equation page 431). On a commercial scale, water is softened by first adding calcium hydroxide to remove the temporary hardness and then sufficient sodium carbonate to correct the permanent hardness and react with the excess of calcium hydroxide that was used. The amounts of the reagents to be used must be determined by an analysis of the water.

If hard water is used in boilers without softening, on the evaporation of the water, a hard scale, known as boiler scale deposits (page 443). Three different substances are found in boiler scale: (1) calcium sulfate; (2) calcium carbonate; (3) magnesium salts. Calcium sulfate, sparingly soluble in cold water, is less soluble in boiling water; it is, therefore, precipitated. Calcium carbonate is precipitated by boiling, if the water contains calcium acid carbonate. Magnesium salts are mostly present as the chloride. They are hydrolyzed by boiling water, forming magnesium hydroxide and hydrochloric acid (equation, page 444)

The conditions referred to in the previous paragraph that sulfates and chlorides of these metals are not removed by boiling are for dilute solutions, but here the conditions are those of a concentrated solution, which explains the seeming contradiction.

Magnesium hydroxide, which forms a part of the scale, has a sort of cementing effect, causing the particles of the scale to form a hard compact mass which adheres to the boiler. This sometimes cracks and the acid acts with the iron, weakening it. Explosions may be caused by the water coming in contact with the superheated iron.

"Boiler compounds," used to prevent the formation of boiler scale, do not prevent the precipitation of these substances, but do have a tendency to hold them in suspension or keep them in a loose state, so that they can be flushed out with water or blown out with steam. Tannic acid is the principal ingredient of "boiler compounds."

Fertilizers. Many of the elements are essential to plant growth. Six are very important: carbon, hydrogen, oxygen, nitrogen, phosphorus, and potassium. Plants obtain carbon from the carbon dioxide of the air and hydrogen and oxygen from the water in the soil. The other elements must be present in the soil in water-soluble form so that they can be absorbed with the water by the roots of the plants. As nitrogen, phosphorus, and potassium compounds are withdrawn from the soil by growing crops they must be replaced. This is done by adding fertilizers. Fertilizers are mixtures of compounds of these three elements.

- 1. Sources of nitrogen. Many of the sources of nitrogen compounds for this purpose have already been referred to, such as, Chili saltpeter, ammonium sulfate, calcium nitrate (air saltpeter), and calcium cyanamide. Organic nitrogenous matter, as dried blood, slaughter-house waste, and manure, is an important source. The organic nitrogen is converted into nitrates by oxidizing bacteria.
- 2. Sources of phosphorus. The source of the phosphorus in fertilizers is usually calcium phosphate. Ground bones are especially valuable because they also contain nitrogen. Likewise, phosphate rock is mined for this purpose in large quantities. Calcium phosphate is nearly insoluble in water, so it would not be

available as plant food until acids in the soil had dissolved it. This would take too long; therefore calcium phosphate is treated with sulfuric acid, forming soluble calcium acid phosphate (equation, page 437). The mixture of sulfate and acid phosphate resulting is known as *superphosphate of lime*. Slag from the steel works sometimes contains enough phosphate to be used to make fertilizer.

3. Sources of potassium. The chief source of potassium compounds has been the Stassfurt mines in Germany (page 407). These salts are used directly in the fertilizer. During the war this source of potassium compounds was shut off, and fertilizers were low in percentage of potash. Wood ashes was used as far as the limited supply would go. The composition of a fertilizer is varied according to the crop to be grown, but always contains some of these three kinds of material, nitrogen, phosphorus, and potassium. Lime is sometimes added to a soil to neutralize its sour condition (page 438).

### MAGNESIUM FAMILY

# Assignment: Chapter XXXV, McPherson and Henderson

Characteristics of family. The metals of this family are members of the same group as the alkaline-earth metals. Magnesium, zinc, cadmium, and mercury constitute the family. Mercury is below hydrogen in the electrochemical series and for that reason has many properties similar to those of copper and silver. It will be studied with them. Magnesium and zinc occupy places well above hydrogen and, therefore, are active metals. They form weaker bases than the alkaline-earth metals and are less active with oxygen and water. Magnesium will liberate hydrogen from boiling water, and red-hot zinc will do the same from steam. Both liberate hydrogen from the acids freely. They are tarnished in the air. Zinc acts upon strong bases, liberating hydrogen.

Magnesium. Magnesium is prepared by the electrolysis of magnesium chloride or carnallite (page 408). The element is a light metal. It burns with a brilliant white light which is rich in rays that affect photographic plates, and in the form of a fine

powder it is used in making flash lights for taking photographs. Mixed with an oxidizing agent like potassium chlorate, it is used in making rockets to light battlefields at night. Some alloys contain magnesium as magnalium; they are used where lightness is required.

Compounds of magnesium. The compounds of magnesium resemble those of calcium in many respects. Magnesium oxide (MgO), a soft bulky powder, is called magnesia. It is unchanged at high temperatures and is used in making crucibles and lining furnaces. It is used in medicine as a mild alkali. Magnesium hydroxide (Mg(OH)<sub>2</sub>) is insoluble in water but is a fairly strong base. Milk of magnesia is magnesium hydroxide; it is used as a laxative. The carbonate (MgCO<sub>3</sub>) is found as magnesite and with calcium carbonate in the mineral dolomite (CaCO<sub>3</sub>.MgCO<sub>3</sub>). Dolomite is used as a building stone. Magnesium sulfate (MgSO<sub>4</sub>) is found extensively as the hydrate; it is called Epsom salt and is used in medicine, in the manufacture of sulfates of sodium and potassium, in tanning, for weighting cloth, and in making paints and laundry soaps. Serpentine, asbestos, and talc are magnesium silicates. Asbestos is used as a covering for pipes, furnaces, and boilers because it is a non-conductor of heat.

Zinc. Like the metals already studied, zinc never occurs free in nature. Its principal ores are sphalerite (ZnS) and franklinite (ZnO.Fe<sub>2</sub>O<sub>3</sub>). Zinc is obtained by roasting the sulfide or carbonate to form an oxide (equations, page 445). The oxide is then mixed with coal dust and reduced to zinc. The boiling point of zinc is low enough to permit the metal to distill over. Commercial zinc contains carbon, arsenic, and iron. Pure zinc is made by dissolving this spelter in hydrochloric acid and electrolyzing the zinc chloride solution.

Zinc has a high luster, but tarnishes in the air; at ordinary temperatures the action with oxygen is superficial, but at high temperatures the metal burns. Water acts with it at high temperatures. Pure zinc acts slowly with the acids to form hydrogen, because the hydrogen collecting on the zinc forms a non-conducting coat which protects the metal from coming in contact with the electrically charged ions of hydrogen from the acid. If, however, impurities are present, like carbon or copper, the hydrogen

molecules are formed on these more negative elements, and the zinc is left free to take ionic charges from the hydrogen. For this reason copper sulfate, which forms copper, is added in making hydrogen with pure zinc. Zinc is used in making alloys, as brass. Galvanized iron is sheet iron coated with zinc to protect it from rust (page 447); this is the largest use of zinc. Sheets of zinc are used for lining sinks. In electric batteries zinc forms one of the poles, and it is used in separating silver from lead (page 516).

Compounds of zinc. The oxide (ZnO), known as zinc white, occurs in nature in impure form; it is prepared by burning zinc. Zinc oxide finds a large use as a white pigment. It is not colored dark by sulfur compounds as white lead is. It is used as a filler in rubber goods, such as automobile tires. Zinc sulfate (ZnSO<sub>4</sub>) forms a hydrate known as white vitriol. It is used in electric batteries. Zinc chloride (ZnCl<sub>2</sub>) has an antiseptic action and is used to preserve wood from decay, as in railroad ties. Copper sulfate and coal-tar creosote are used for this purpose also (page 448).

### **EXERCISES\***

- 1. Discuss the properties of the alkaline-earth metals.
- 2. Give the mineral name, chemical name, and formula for five calcium minerals.
  - 3. What is lime? How is it prepared? What are its uses?
  - 4. What is slaked lime? Give its uses.
  - 5. What is mortar? Explain how it sets.
- 6. How is bleaching powder made? What is its formula? How does it act as a bleaching agent?
- 7. Name five natural varieties of calcium carbonate. What is precipitated chalk? Write the equation for making it.
  - 8. What is plaster of Paris? How is it made? What are its uses?
- 9. What is hard water? Give the cause of the two kinds of hard water.
  - 10. How is hard water softened?
  - 11. What causes boiler scale? Give its composition.
  - 12. How is calcium carbide made? What are its uses?
  - 13. How is calcium cyanamide made? What is its use?
- 14. Give the flame coloration imparted by calcium, strontium, and barium salts.
- 15. What is a fertilizer? Name the three constituents of a fertilizer and their chief sources. Is lime a fertilizer?

<sup>\*</sup>Prepare this set of Exercises and hold it until those for Lessons XXII, XXIII, XXIV, and XXV are also prepared and then send all five sets to the School.

- 16. Give the properties of the magnesium family.
- 17. How is magnesium made? What are its uses?
- 18. Describe the metallurgy of zinc.
- 19. State the properties and uses of zinc.
- 20. How is pure zinc made?
- 21. Why is zinc used in galvanizing iron? How is iron galvanized?
- 22. How is wood preserved?
- 23. Give chemical name, formula, and use for each of following: white vitriol, sphalerite, zinc white, Epsom salt, gypsum, quicklime, and dolomite.
  - 24. Answer questions 4, 6, 7, 8, 11, 12, and 13, page 438.
  - 25. Solve problems 14, 15, 17, 19, and 20, page 439.
  - 26. Answer questions 5, 6, 7, 8, 9, 11, and 12, page 450.
  - 27. Solve problems 14, 15, 16, and 17, page 450.

### LESSON XXII

### COLLOIDS; ALUMINIUM

#### COLLOIDS

# Assignment: Chapter XXX, McPherson and Henderson

The colloidal state. Substances which assume a jelly-like form are known as *colloids*. The word means glue. Many organic substances are of this nature, such as gelatin, soap, eggyolk, dyes, and the casein of milk. Silicic acid, hydroxides, like aluminium, and sulfides, like arsenic and nickel, are inorganic substances that tend to assume the colloidal state.

There are two kinds of colloidal states. One, in which the substance seems to be in solution, the other in which it forms a jelly with the water. A dilute solution of water glass, to which dilute hydrochloric acid is added, remains apparently unchanged for a time, but, on standing, a jelly-like precipitate of silicic acid forms. The clear liquid just referred to is not a true solution of silicic acid. This is shown by passing a ray of light through it in a dark room (page 383). The path of the light is visible, as it is if passed through the air in a dark but somewhat dusty room. The path of the light is visible because small particles of matter reflect the light. A true solution, as sodium chloride, shows no visible path under similar conditions.

The first colloidal state, where the substance appears in near solution, is called *sol*, or *hydrosol*. The second state, in which the

jelly-like form exists, is known as gel, or hydrogel. The essential difference between a true solution and a hydrosol seems to be due to the size of the particles. In true solutions the particles (molecules) are so small as not to be able to reflect the light as the rays pass through. In the next state they are large enough to reflect some of the light but not large enough to interfere with the transparency of the liquid. This is the state of colloidal solution. In this state, the liquid does not obey the laws of freezing-point lowering as do true solutions. In another state the particles are large enough to give an opaque or milky appearance to the liquid, but too small to be filtered off or to settle. This may be called a colloidal suspension. Suspensions settle after a time, and precipitates settle quickly. The difference, then, is a matter of the size of the particles.

Changing conditions can cause the hydrosol to become a hydrogel. This change is called coagulation. Some coagulations are reversible and some are not. Gelatin and water form a hydrosol when warm and a hydrogel when cold as often as desired. The white of an egg beaten up with water is a hydrosol. Heating coagulates it, and this change is not reversible. The addition of an electrolyte will cause the coagulation of some colloids which have electric charges upon them. Colloidal gold is a negative colloid and is coagulated by the positive ion of a salt; ferric hydroxide is a positive colloid and the negative ion of the salt coagulates it (page 383).

Colloids are prepared by two methods: (1) by powdering solids; (2) by imperfect precipitation. See the illustration and examples on page 384. When hydrogen sulfide is passed into a solution of arsenious acid, the sulfide (As<sub>2</sub>S<sub>3</sub>) is formed, but remains in colloidal suspension. It is coagulated by adding an electrolyte in the form of a solution of a salt.

Colloids are not a special kind of substance, but any substance may assume the colloidal state, just as it may assume the liquid or solid state or the state of a true solution. No sharp distinction can be drawn between the different classes. In colloids the molecules are bunched together without any order; in crystals the molecules assume an orderly arrangement. In the hydrogels the bunches of molecules inclose water, forming the jellies.

Many important industries are based upon the properties of colloids. Soap solution is a colloid and owes its cleansing action mostly to this property. The decolorizing of sugar by charcoal is due to the colloidal nature of the coloring matter, the colloid being absorbed by the charcoal. Colored glasses have colloidal matter suspended in them. Silver salts are colloidally suspended in collodion. The use of aluminium hydroxide in the purification of water (page 457) and as a mordant for dyes (page 458) depends upon its colloidal nature. Rubber is a colloid, as are gums, waxes, glues, cements, and bread dough.

A similar condition exists in emulsions. Here we have two liquids not soluble in each other, as oil and water. If the particles can be kept small enough, a permanent emulsion results. If oil and vinegar are beaten together (French dressing), we have a temporary emulsion. If the yolk of an egg (colloidal) is added, a permanent emulsion (mayonnaise dressing) results. Milk is a somewhat imperfect emulsion as the cream separates out. For the emulsion to be stable, it is necessary that a third substance of a colloidal nature be added. Soap solution admirably serves the purpose of keeping the small particles of oil from joining to form larger ones and so keeps oil emulsified.

#### **ALUMINIUM**

# Assignment: Chapters XXXVI and XXXVII, McPherson and Henderson

The group. Aluminium is a member of Group III. Boron is the non-metallic member of the group and has already been studied. Aluminium is the only metal of the group that occurs abundantly, the others being rare, and only aluminium will be studied. It is a very useful metal and many of its compounds find wide application. The metals of the group are trivalent. They form weak bases, many of whose salts are hydrolyzed in solution. Their oxides are known as earths.

Occurrence. Aluminium is the most abundant metal, more so than iron, but it is difficult to obtain it from some sources. It is mostly found in the form of silicates which are hard to decompose. Feldspar and clay both contain aluminium, but it is not obtained from these sources in any quantity. Bauxite (Al<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O and

Al<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O) and cryolite (Na<sub>3</sub>AlF<sub>6</sub>) are used in preparing it commercially. The element is called aluminum as well as aluminium; the former word is most used in commerce.

Preparation. The metal is prepared by the electrolysis of a solution of bauxite in fused cryolite. This process is described on page 453. The method was devised by Hall in 1886. Prior to that time the metal was rare. Cheap aluminium depends upon cheap electric energy, and therefore its preparation is one of the electrochemical industries at Niagara Falls.

Properties and uses. Aluminium is a light, white metal. It is strong and a good conductor of heat and electricity. Moist air tarnishes it slightly, forming a thin film of oxide which prevents further action; boiling water has little, if any, effect upon it for the same reason. The metal will burn in air. It unites with oxygen at high temperatures liberating much heat (page 454). It is, therefore, a good reducing agent, and as such it is used in the metallurgy of some metals—the Goldschmidt reduction process. The thermite process, used for welding steel rails, is an application of the same principle. It is described on page 455.

Dilute acids act upon it, liberating hydrogen, though sulfuric acts very slowly and nitric almost not at all, because of the insolubility in these two acids of the film of oxide. Concentrated and hot sulfuric acid acts with it as with other metals:

# $2Al+6H<sub>2</sub>SO<sub>4</sub>\rightarrow Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>+6H<sub>2</sub>O+3SO<sub>2</sub>$

Concentrated nitric acid has almost no action on it, but aluminium in alloys dissolves readily in slightly diluted nitric acid. Strong bases react with it to form aluminates and hydrogen:

## 2Al+6KOH→2K<sub>3</sub>AlO<sub>3</sub>+3H<sub>2</sub>

Aluminium is well adapted to many construction purposes, because of its lightness, strength, and non-corrosiveness. It is used in the construction of airplanes; cooking vessels are now largely constructed from it; as a conductor of electricity it is used as trolley wires. A powder form is used as a paint for metal surfaces. Alloys are made with it. With copper it forms aluminium bronze and with magnesium it forms magnalium.

An interesting use of aluminium is in cleaning silverware. The tarnish on silver is usually silver sulfide. When silver spoons, knives, etc., are placed in contact with aluminium, as in a stew pan, and covered with water, which is then boiled, the aluminium replaces the silver, first forming aluminium sulfide. This at once hydrolyzes to form aluminium hydroxide. The silverware is left with a clean surface, but needs polishing to give it the silver luster.

Compounds of aluminium. Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) occurs as emery or in pure form as corundum. Colored with impurities it forms precious stones, as sapphire, ruby, topaz, and amethyst. Artificial sapphires and rubies have been made which are said to be equal to natural stones as jewels. All forms are hard, and emery is used for grinding, as in emery wheels.

Aluminium hydroxide (Al(OH)<sub>3</sub>) forms as a colloidal precipitate when ammonium hydroxide is added to an aluminium salt in solution. It is insoluble, but hard to filter. Heating drives out water, forming the oxide. The special property of aluminium hydroxide to be noted is that it will react with both acids and bases; like antimony hydroxide, it is amphoteric. See the equations on page 457 showing its action with hydrochloric acid and with sodium hydroxide. With the latter it forms salts of sodium known as aluminates (Na<sub>3</sub>AlO<sub>3</sub>).

Aluminium sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) is cheap and is used in water purification, in making alum, in dyeing, and in making paper. Alums are double sulfates; two molecules of sulfuric acid have three of their hydrogen atoms replaced by aluminium and one by potassium to form common alum. Other trivalent elements replace aluminium, and other alkali metals replace potassium to form other alums (page 459).

Aluminium nitride (AlN) is formed when the metal and nitrogen are heated together at high temperatures. The nitride reacts with water to form aluminium oxide and ammonia (page 461). This reaction serves as a method for fixing atmospheric nitrogen. Other methods of utilizing atmospheric nitrogen have been mentioned in previous lessons; all of them are summarized on pages 461 and 462.

Uses of aluminium hydroxide. Because of its colloidal nature, aluminium hydroxide is valuable in purifying water (pages 71 and 457). The coagulation of the colloid causes it to settle, and as it

does so, it carries with it suspended matter. The hydroxide is formed by dissolving in the water some cheap salt which hydrolyzes. Usually enough basic matter is in the water to combine with the sulfuric acid set free in hydrolysis:

$$Al_2(SO_4)_3+6H_2O\rightarrow 2Al(OH)_3+3H_2SO_4$$

Otherwise a base, like calcium hydroxide, must be added.

Aluminium hydroxide is widely used in the dyeing industry. Either because of its colloidal nature or because of its amphoteric property, it absorbs or combines with many of the dyes (which are either weak acids or weak bases). The dyes are organic compounds prepared from coal-tar derivatives. Many are not fast dyes with cotton; in such a case the cloth is dipped in a solution of an aluminium salt and exposed to steam. This forms aluminium hydroxide, which in one way or another holds the dye fast. A substance which serves to fix the dye on the fiber is called a mordant.

Baking powders. As was seen in the preceding paragraph, aluminium salts hydrolyze. This reaction is complete if a salt of a weak acid is used. When a solution of sodium carbonate is added to one of aluminium chloride, the expected aluminium carbonate does not precipitate. If it forms, it is hydrolyzed to aluminium hydroxide (equations, page 460). Use is made of this reaction in making alum baking powders.

Baking powders are of three types. They all contain starch or flour and sodium bicarbonate. The soda furnishes the carbon dioxide; the starch keeps the powder dry and serves to dilute it. They differ in the constituent which is used to liberate the carbon dioxide. Alum, cream of tartar, and calcium acid phosphate are the three substances used for this purpose. The equations in the three cases are as follows:

$$2KAl(SO_4)_2 + 6NaHCO_3 \rightarrow 2Al(OH)_3 + 3Na_2SO_4 + K_2SO_4 + 6CO_2 \\ KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2 \\ CaH_4(PO_4)_2 + 2NaHCO_3 \rightarrow CaHPO_4 + Na_2HPO_4 + 2H_2O + 2CO_2 \\$$

Baking powders are used to furnish carbon dioxide, which, expanding, makes the dough light. Sometimes soda and sour milk are used.

Aluminium silicates. A number of these silicates, which are found in nature and are useful substances, are mentioned on page 464. Clay products find a wide use in building operations and in the manufacture of pottery. Common brick and tile are made from clay without chemical change, except the conversion of iron compounds to ferric oxide, when the clay is heated. This gives these objects a red color. Vitrified brick is made by being heated high enough to partially fuse the clay, forming a kind of glass.

Pottery. Pottery includes fine chinaware and crude porcelain. The methods of manufacture are essentially the same and consist of three steps: (1) preparation of the body, or bisque; (2) glazing; (3) decorating. The different kinds of bisque, from very porous to non-porous, are made by varying the quantities of clay and feldspar used. The glaze is used to render the ware nonporous and to give a smooth surface; it is a fusible glass melted into the body of the object. Silica, feldspar, and metallic oxides are used in making the glaze. They are made into a paste into which the bisque is dipped; the objects are then fired in a kiln to fuse the glaze to the body. Metallic oxides or colored glasses made from metallic oxides and silica, that is, silicates, are the pigments used in decorating china.

Cement. Portland cement is the most important cement. It is made by powdering limestone and clay or shale together and heating the mixture to a clinker in a furnace. This clinker is then ground to a powder and is the cement. Gypsum is sometimes added to retard the setting. Cement is a silicate, principally of calcium and aluminium. Smaller amounts of iron and magnesium silicates are present (table on page 466). Any materials furnishing these ingredients can be used to make cement. Blast-furnace slag is frequently used. Cement will harden under water as well as in air. This setting of cement is due to reactions not fully understood. Apparently hydrolysis takes place first, and then hydrates are formed which crystallize into a hard mass. The use of cement is growing greater every year. Mixed with crushed stone, it forms concrete, which is used for various kinds of construction, paved roads, bridges, walls of buildings, and even for hulls of ships.

### **EXERCISES**

- 1. What is meant by a colloid?
- 2. What is a hydrosol; a hydrogel?
- 3. What is the nature of the colloidal state?
- 4. How are colloids prepared?
- 5. Give all the industrial applications of colloids you can.
- 6. What are emulsions? Give examples.
- 7. Describe the Hall method for making aluminium.
- 8. What are the properties and uses of aluminium?
- 9. Describe the thermite welding process.
- 10. What are alum, corundum, ruby, alundum, sapphire, emery, bauxite, cryolite, feldspar, mica, clay, and Fuller's earth?
- 11. Explain the use of aluminium hydroxide in purifying water; as a mordant in dyeing.
  - 12. Discuss the three kinds of baking powders.
  - 13. Give all the methods for fixing atmospheric nitrogen.
  - 14. Discuss the manufacture of white pottery.
  - 15. Discuss the manufacture and setting of cement.
  - 16. Answer questions 2, 3, 4, 5, 7, and 9, page 462.
  - 17. Answer questions 10, 11, 12, 13, and 14, page 463.
  - 18. Solve problems 16 and 17, page 463, and 7, page 468.
  - 19. Answer questions 1, 2, 3, 4, and 5, page 468.

# LESSON XXIII

### **IRON**

# Assignment: Chapter XXXVIII, McPherson and Henderson

The family. Iron, cobalt, and nickel occur in the eighth group of the periodic system. Their atomic weights are nearly equal and their properties very similar. They have a valence of two and three in their compounds. Iron is by far the most abundant and important of the three. In fact, it is the most widely used of all the metals and is more abundant than any other except aluminium. It is mostly used in the metallic form as is nickel. These elements are not found free in nature, but in the form of oxides, sulfides, and carbonates. Elementary iron has been found in meteorites; few rocks or soils are free from iron; it is a constituent of the haemoglobin of the blood and of the chlorophyll of plants.

Iron. Pure iron is seldom prepared and is too soft for most uses. It can be prepared by the electrolysis of iron sulfate or by

reducing iron compounds with hydrogen. Practically pure iron can be obtained by the open-hearth method (page 478). This is especially adapted to use in electromagnets. The iron of commerce contains small percentages of other elements, which modify its properties somewhat. Carbon, silicon, phosphorus, manganese, sulfur, and oxygen are found in iron. Carbon is always present in varying amounts and in varying forms: as graphite, which has crystallized from the iron on cooling; in solid solution in the iron; as carbides, such as Fe<sub>3</sub>C. These carbides may be in solid solution or separated out. The state of the carbon depends upon the conditions of manufacture and cooling of the iron. For these reasons iron exists in three recognized varieties, cast iron, wrought iron, and steel.

The metallurgy of iron. In making iron, large and rapid production is a necessary requirement as well as a product of the desired composition. Cast iron is the variety that is always made directly from the ore. The materials used are of four kinds, the ore, carbon, hot air, and flux. The products of the operation are cast iron, slag, and the gas.

- 1. Ores. The ores most used are oxides and carbonates of iron (page 471). A common iron mineral (FeS<sub>2</sub>) is used for its sulfur in making sulfuric acid, but it is not a satisfactory iron ore, because it is difficult to get iron of sufficient purity from it. The ores of iron contain impurities which may be classified as acidic or basic in nature. The oxides usually have acidic impurities, as sand, clay, etc. The carbonate ore contains other carbonates, as limestone, and is basic. Sulfides and phosphates are often present.
- 2. Carbon. Carbon is used as the fuel and reducing agent. However, the carbon does not directly reduce the iron oxide. It first burns to carbon dioxide. This is reduced to carbon monoxide, which in turn reduces the iron oxide:

### $Fe_3O_4+4CO\rightarrow 3Fe+4CO_2$

This carbon dioxide is again reduced by the carbon to the monoxide. The monoxide mixed with nitrogen escapes from the furnace. Coke is the form of carbon usually used, although formerly wood charcoal was used. Coal cannot be used as it uses up too much heat in giving off its volatile matter.

- 3. Hot air. Hot air is used to maintain a high temperature by supplying oxygen to burn the fuel. A strong blast of hot air is forced into the lower part of the furnace during its operation.
- 4. Flux. In order that the iron may flow free from the earthy matter, it is necessary that these earthy impurities be converted into substances which will melt and flow off. This is done by making them into a sort of glass. Glasses are silicates of metals; that is, they are salts composed of a basic and acidic constituent. The nature of the flux needed to form this glass, then, depends upon the nature of the impurities in the iron ore. If the ore contains sand or clay, it is necessary to add a basic flux, such as limestone (CaCO<sub>3</sub>). If, however, limestone is the impurity in the ore, then an acid flux must be used, as sand or feldspar. When heated, the impurity and the flux combine and form a liquid glass, or slag.

The slag is essentially a calcium-aluminium silicate, and is difficult to fuse. It is produced in that region of the furnace where the temperature is about 1200° C. This is the temperature at which the cast iron becomes liquid enough to flow freely. If the slag were produced higher up in the furnace, it would contain some of the iron as iron silicate, and the iron would be lost. The slag is lighter than the iron and floats on top, where it is continually drawn off through a small opening in the furnace. The iron is tapped off at intervals from an opening lower down.

The gas, consisting mostly of carbon monoxide and nitrogen, is carried off by the downcomer pipes. This gas is used for heating the hot blast and as a fuel to operate the engines that furnish power. The description of the blast furnace (pages 473 and 474) should be carefully studied. If opportunity ever offers, the student should observe a blast furnace in operation.

Cast iron. The varieties of iron vary in composition, mostly with respect to the carbon content, but this is not a good guide in distinguishing them from one another. The carbon content of one form overlaps that of another. Some steels contain more carbon than some cast irons. Generally, however, cast iron contains more carbon than the other varieties. The properties of the forms of iron depend much upon their method of manufacture. We may say that cast iron is the product of the blast furnace.

Frequently it is not cast in molds, but, while still hot, is converted into steel and then into rails or other forms for ultimate use. Sometimes it is cast in molds by machinery or by allowing it to run into troughs made in sand (Fig. 187, page 474). These castings are called pigs, because the arrangement of the molds suggests suckling pigs and the mother hog.

Cast iron contains from 2 to 5 per cent of carbon, sometimes nearly as much silicon, and smaller amounts of manganese, phosphorus, and sulfur. Two kinds of cast iron occur, depending upon the form in which the carbon exists. If suddenly cooled, the carbon, as iron carbide, remains in solid solution. This iron is homogeneous and very brittle. It is called white, or chilled, cast iron. If the cooling is slower, the carbon separates as graphite, which appears as black scales. This form is called gray cast iron. Cast iron has a lower melting point than pure iron. It expands in casting and is used for making stoves, radiators, and some parts for machinery. It is rigid, but not elastic, so breaks easily. It is the starting point for making wrought iron and steel.

Wrought iron. This is the purest of the three varieties. It is made by burning out the carbon and other impurities in a puddling furnace, so called because the iron is stirred with iron rods (as in a puddle). As it becomes pure, the iron stiffens and is withdrawn in balls on the ends of the stirring rods. Oxide of iron is added to the lining of the furnace to supply oxygen. Wrought iron melts at a higher temperature than cast iron, is soft, and has a fibrous structure, while cast iron has a granular structure. It is not produced on a large scale, as steel serves for most of the purposes for which it could be used.

Steel. This variety of iron is almost free from silicon, phosphorus, and sulfur, but contains carbon from traces up to 2 per cent, as may be desired for different uses. Steel has a very fine granular structure. It is elastic and hard; it can be forged, cast, and rolled. It is the product of the Bessemer or the open-hearth process.

The Bessemer process was invented by Kelly, an American, and by Bessemer, an Englishman, at about the same time. It is usually used at the present time for irons which contain little phosphorus; the converter is then lined with fire clay or silica (study description on page 477). A modification of this process

has been used for irons containing considerable phosphorus; the converter is then lined with lime and magnesia, which will form a slag containing the basic phosphate of calcium. This is known as the basic-lining, or Thomas-Gilchrist, process.

The open-hearth process can be used for both kinds of iron. In this country the furnace is lined with a basic substance like lime and magnesia and is sometimes called the basic open-hearth. The furnace can be lined with sand and used for irons that contain little or no phosphorus. Gas or oil is used as the fuel to heat the open-hearth furnace. The basic open-hearth method removes all but traces of phosphorus and sulfur from the steel. A better grade of steel can be made by this process as better regulation is possible (pages 478 and 479).

Crucible steel is used in making sharp tools. It is made from other steel by melting it in a crucible with the desired amount of pure carbon. A high-grade tool steel is made now in electric furnaces, the current being used only to melt the steel.

Tempering. Steel contains carbon in the form of the element or in the form of iron carbide (Fe<sub>3</sub>C) dissolved in the iron. When the steel is suddenly cooled, no changes take place, and a solid solution results. This is hard and brittle. If the steel is cooled slowly, some of the carbide (Fe<sub>3</sub>C) separates out as crystals, until at 700° C. only 0.9 per cent carbon remains in solution. Under this condition, the solid solution forms a mixture of pure iron and iron carbide. The pure iron is soft, the carbide is hard. If such steel is heated for tempering, the amount of softer material formed depends upon the temperature and the rate and the time of cooling. Steels are tempered to different degrees of hardness for different uses (page 481).

Steel alloys. Many elements as well as carbon are added to steel to vary its properties. The elements most frequently used are manganese, silicon, nickel, chromium, tungsten, vanadium, and titanium. These mixtures are called alloy steels. A list of them and their composition and uses is found on page 481. Aluminium, vanadium, and titanium are used as steel purifiers because they combine with the oxygen and the gases left in the iron, completing the reduction and preventing the presence of gases, which causes blowholes.

Chemical properties of iron. Iron is above hydrogen in the electrochemical series of the metals. It acts readily with acids, forming hydrogen. With dilute acids, the hydrogen is almost pure; with concentrated acids, the carbide present is affected and hydrocarbons are formed. Pure iron does not rust in cold water, but ordinary iron does. The rust consists mainly of hydrated ferric oxide (3Fe<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O). The presence of carbon dioxide hastens the speed of the action. Iron rust is porous and also tends to scale off, so it does not protect the metal from further action as does zinc rust. Iron burns with oxygen and acts with superheated steam to form Fe<sub>3</sub>O<sub>4</sub>. A superficial layer of this will protect the iron from the action of the air. Duriron and tantiron, which are used for acid containers and do not rust, are silicon alloys.

Compounds of iron. Iron forms two series of compounds, one with a valence of two, and one with a valence of three. The bivalent compounds are called *ferrous*, the trivalent, *ferric*. The more important iron compounds are described on pages 482 to 485. An important property of iron compounds is their ability to be oxidized from the ferrous to the ferric state and reduced from the ferric to the ferrous condition.

Moist air will change ferrous compounds to ferric:

$$2\text{Fe}(OH)_2 + O + H_2O \rightarrow 2\text{Fe}(OH)_3$$

Any good oxidizing agent may be used as the source of the oxygen, such as nitric acid or potassium permanganate. In order to get a simple oxidation, the presence of the acid having a common anion with the salt is necessary. If nitric acid oxidizes ferrous chlorides the equations are:

$$2HNO_3\rightarrow H_2O+2NO+3[O]$$
  
 $6FeCl_2+3[O]+6HCl\rightarrow 6FeCl_3+3H_2O$ 

adding gives

$$2HNO_3+6FeCl_2+6HCl\rightarrow 4H_2O+2NO+6FeCl_3$$

Chlorine will convert ferrous salts to ferric:

This is termed oxidation just as if oxygen itself were used. The

term oxidation is applied to any reaction when the valence of the positive ion is increased.

Nascent hydrogen, hydrogen sulfide, and some other substances will reduce ferric salts to the ferrous state:

## FeCl<sub>3</sub>+[H]→FeCl<sub>2</sub>+HCl

When the valence of the positive ion is decreased, the action is called reduction. Oxalic acid is a reducing agent and removes iron rust (ferric oxide) by reducing it to ferrous compounds, which wash out. Iron compounds are used in blue printing (page 488) and in some inks (page 489). Ferrous sulfate is used as a disinfectant, to destroy weeds, and in purifying water.

#### **EXERCISES**

- 1. Name the elements of the iron family. What are the family properties?
  - 2. How is pure iron made? What are its properties?
  - 3. Discuss the occurrence of iron and name the principal iron ores.
  - 4. Discuss the four materials used in making cast iron.
  - 5. How is the kind of flux to be used determined?
  - 6. Describe the blast furnace.
  - 7. What is the slag? What is its use in the blast furnace?
- 8. What purpose does carbon serve? What chemical changes take place in reducing the iron?
  - 9. What gas escapes from the blast furnace? What is its use?
  - 10. State the properties of cast iron. How are the two kinds formed?
  - 11. What are the properties of wrought iron? How is it made?
  - 12. Describe the Bessemer process for making steel.
  - 13. Describe the open-hearth process. What are its advantages?
  - 14. How is crucible steel made? What is its use?
  - 15. Discuss the tempering of steel.
  - 16. Discuss the steel alloys.
  - 17. Give the chemical properties of iron.
  - 18. Give two examples to show the oxidation of ferrous to ferric iron.
  - 19. Define oxidation and reduction in this broader sense.
- 20. What are the properties and uses of nickel? Describe nickel-plating.
  - 21. Answer questions 2, 3, 5, 6, 8, and 11, pages 491 and 492.
  - 22. Solve problems 4, 12, and 13, pages 491 and 492.

# LESSON XXIV

# THE COPPER AND PLATINUM FAMILIES

Assignment: Chapters XXXIX and XLIII, McPherson and Henderson.

Introductory. In this lesson we will study the metals copper, silver, and gold, which belong to the second family of Periodic Group I. Mercury will be studied with these metals, because, owing to its position in the electrochemical series, it is very similar to them in properties, though not of their family. Gold, while belonging to this family, is usually studied with the platinum metals, which find a place in Group VIII. Gold is like platinum in its action toward oxygen and the acids.

All these metals may be properly considered together because of their non-activity toward dilute acids. They are all sufficiently inactive so that they are found in the free state in nature. Copper, silver, and mercury are dissolved by the oxidizing action of nitric acid and hot concentrated sulfuric acid, while gold and platinum metals are not. They are dissolved by the action of aqua regia, however. Silver is a univalent metal. Copper and mercury form univalent and bivalent compounds; gold acts as a univalent and trivalent element; platinum is bivalent and quadrivalent. Silver, gold, and platinum are known as the "noble metals."

Metallurgy of copper. Copper ores are of three kinds: (1) native copper, which occurs in the Lake Superior region; (2) oxygen ores, which are the oxides and carbonates, as cuprite (Cu<sub>2</sub>O) and malachite (CuCO<sub>3</sub>.Cu(OH)<sub>2</sub>); (3) sulfur ores, which are frequently double sulfides like bornite (Cu<sub>3</sub>FeS<sub>3</sub>) but are not always such since chalcocite (Cu<sub>2</sub>S) is found also.

Native copper ore is ground and washed to separate the rock from the copper. The powdered copper is then melted with a flux. The carbonates form oxides when heated and the oxides must be reduced with coal. It is more difficult to obtain copper from sulfur ores, as they cannot be reduced by heating with carbon. Sulfur ores must be heated with a siliceous flux to convert the iron to a slag. The matte, a mixture of copper and iron sulfides, collects under the slag. Sometimes the matte is made in a small blast furnace. The matte is converted to blister copper

by a process similar to the Bessemer process for iron. The iron forms a slag with the silica, which is added. Blister copper must be refined by electrolysis (page 496).

Properties and uses of copper. The uses of copper depend upon its inactivity toward water, dilute acids (except nitric), and oxygen at ordinary temperatures and upon the fact that it is malleable, ductile, and a good conductor of electricity (page 497). Copper is an important constituent of many alloys (see table, page 497). In addition to the uses mentioned on page 497, it was formerly used for making tools and castings; it is used sometimes for making kettles, boilers, and tubes for washing machines; great quantities are used in electrical plants and appliances; it is used in electrotyping. The United States furnishes over half of the copper used.

Compounds of copper. Cuprous and cupric compounds are known. Copper is univalent in the former and bivalent in the latter. The cupric compounds are much the more common and important. Cupric sulfate, when crystallized with water of hydration (CuSO<sub>4</sub>.5H<sub>2</sub>O) is called *blue vitriol*. It is used in copperplating; in batteries; as a mordant in dyeing; to destroy algae in drinking water; mixed with milk of lime (Bordeaux mixture), to spray grape vines, fruit trees and vegetables; in making insecticides; in copper refining; and as a remedy in hoof disease. The use of copper sulfate in electric cells (page 500) should be given special attention.

Mercury. The chief ore of mercury is cinnabar (HgS). It occurs native as well. It is easily obtained by heating the ore with carbon; the mercury is volatile and boils over. It is a liquid at ordinary temperatures. It acts much like copper toward acids and water but is somewhat less active toward oxygen. The metal is used in thermometers, barometers, and in making alloys; its alloys are called *amalgams*. It is used in the metallurgy of gold and silver, extracting them from the crushed ores by forming amalgams. The finely divided element is used in medicine (blue pills).

Two series of salts are formed, mercurous (univalent) and mercuric (bivalent). The chlorides are both important. Mercurous chloride is the common drug *calomel* (HgCl). It is a white insoluble salt and is used as a purgative, usually mixed with

sodium bicarbonate to prevent acids from converting it to the mercuric form. Mercuric chloride (HgCl<sub>2</sub>), corrosive sublimate, is very poisonous. It is used in dilute solutions as an antiseptic in dressing wounds and as a means of killing bacteria in laboratories. Serious cases of poisoning occur by taking the salt by mistake. Mercuric sulfide (HgS) occurs in a black and a red form. The red form, known as vermillion, is used as a pigment in paints. Mercuric fulminate (Hg(ONC)<sub>2</sub>) is used as the explosive in percussion caps.

Silver. Native silver is found alloyed with gold and copper, usually scattered through rocky material. Silver sulfide (Ag<sub>2</sub>S) is the chief source of silver. It occurs alone or mixed with lead sulfide (PbS). The metallurgy of silver is dependent upon the substances with which it occurs. If alloyed with gold, it is a product of the extraction of gold (page 550); if it occurs as a sulfide with lead, it is obtained in crude form from the lead by the Parkes process (page 516). The crude silver is refined by parting with sulfuric acid or by electrolysis. If sulfuric acid is to be used, the silver is first cupelled (page 504) to oxidize the baser metals; sulfuric acid dissolves the silver from the gold; finally the silver is precipitated from the sulfate by copper. In refining by electrolysis silver nitrate is used as the electrolyte.

Properties of silver. While silver is similar to copper in many respects, it does not act with oxygen. Ozone will oxidize it. It is below copper in the electrochemical series and generally is less active, yet its oxide is quite basic, absorbing carbon dioxide from the air. Its oxide, like that of mercury, can be decomposed by heat. Sulfur and sulfur compounds (eggs, mustard, rubber, perspiration) quickly tarnish silver. Dilute acids and fused alkalies do not act with it. It is used in alloys for coins and tableware, and mirrors are backed with it. Many objects made of cheaper metals are plated with silver by electrolysis; potassium silver cyanide is usually used as the electrolyte.

Silver compounds. The nitrate of silver (AgNO<sub>3</sub>) is known as *lunar caustic*. It is used in surgery because of its corrosive action on flesh. The halogen compounds with silver are used in photography. The chloride, bromide, and iodide of silver are all insoluble in water and undergo a change of color and composition

when exposed to sunlight. The bromide and iodide are most used and require a developer (reducing agent) to bring out the image. The developers are organic compounds. (See "Photography," page 508.)

Gold. Most of the gold is found in the free state. There are three ways of mining gold. Placer (c is pronounced like s) mining is the oldest method, but hydraulic and vein mining are more used now (page 550). The extraction of gold from its ore can be accomplished by the amalgamation or the cyanide process (page 550). The cyanide process is successful with ore containing small percentages of gold. Sometimes it is used to extract gold from the "tailings" left from other processes. The introduction of the cyanide process greatly increased the gold production of the world. Gold extracted in these ways contains other metals, as silver, lead, copper. It is refined by electrolysis, cupellation, parting with sulfuric acid, or by a combination of the last two methods (pages 550 and 551).

Properties of gold. Gold is an inactive element. It does not combine with oxygen, nor the common acids. Aqua regia dissolves it, and fused alkalies attack it. It reacts with free chlorine and bromine. It is a soft metal, and to give it hardness, it is alloyed with silver or copper. Gold compounds are decomposed by heat. Other metals replace gold from solutions of its salts, and reducing agents likewise precipitate the gold. It is precipitated in the form of a brown powder. Mixed with oil, it is used in this form for decorating china. When fired, the gold assumes its common yellow color. It is used mostly for coins and jewelry.

The platinum family. Two sets of three metals each occur in Group VIII after the iron family. The first have atomic weights about 100. Palladium is the most important of the three. It is distinguished by its ability to absorb large quantities of hydrogen and it is used for this purpose in gas analysis. The next set have atomic weights near 200. Platinum is the most important of this set. All six are found alloyed together in nature and closely resemble each other in properties. They are known as the platinum family.

Platinum. Most of our platinum comes from the Ural mountains in Russia. It is separated from the sand by washing. Native platinum is 60-84 per cent platinum. The other mem-

bers of the family and gold constitute the rest. To separate the platinum, the alloy is dissolved in aqua regia. Ammonium chloride is used to precipitate the platinum (page 545). Platinum is an inactive element, being acted upon only by aqua regia, the fused alkalies, and chlorine, and it has a high melting point. For these reasons it is much in demand for making laboratory utensils. Large platinum dishes are used to concentrate chamber sulfuric acid.

It is used as a catalytic agent, and is prepared in a very finely divided condition for this purpose. It is so used in making sulfuric acid by the contact process and in making formaldehyde from methyl alcohol. Platinum has the same coefficient of expansion as glass and was formerly used in light bulbs. It is used in jewelry, photography, and dentistry. In fountain-pen points an alloy with iridium is used because of its greater hardness. Many substitutes are being devised for platinum because of its great cost. It is more than twice as costly as gold, and the price is increasing.

### **EXERCISES\***

- 1. Discuss the metallurgy of copper.
- 2. State the properties of copper.
- 3. How does copper react with hydrochloric acid; dilute sulfuric acid; dilute nitric acid; fused alkalies; oxygen; water; hot concentrated sulfuric acid? Write equations where action occurs.
  - 4. Give the uses of copper. Name its alloys.
  - 5. What are the uses of copper sulfate?
  - 6. Explain the action of the Daniell cell.
  - 7. How is mercury obtained from its ore?
  - 8. Give the properties of mercury; also the uses.
  - 9. How does it act with the reagents named in question 3?
- 10. What are calomel and corrosive sublimate? Give their properties and uses.
  - 11. Discuss the occurrence and the metallurgy of silver.
  - 12. Give the properties of silver; also the uses.
  - 13. Give the reactions of silver with the reagents in question 3.
  - 14. Discuss fully the subject of photography.
  - 15. Discuss the mining, extraction, and refining of gold.
  - 16. Give the properties and uses of gold.
  - 17. How does gold act with reagents in question 3?
  - 18. Give the occurrence and the extraction of platinum.
  - 19. Discuss the properties and the uses of platinum.
  - 20. Give a use for iridium, osmium, palladium, and lunar caustic.
  - 21. Answer questions 1, 2, 3, 4, and 5, page 509.
  - 22. Answer questions 6, 7, 8, 9, 10, and 12, page 510.
  - 23. Solve problems 16, 17, and 18, page 510.

# LESSON XXV

# OTHER METALS

Assignment: Chapters XL, XLI, XLII, and XLIV, McPherson and Henderson.

Introductory. Several metals remain to be studied, and certain others need a brief reference. They are discussed in this lesson, but they do not belong together in the periodic grouping, nor are they closely related in properties. Tin and lead are somewhat alike, so are manganese and chromium, while radium and uranium have a similarity of properties.

Tin. The principal ore of tin is the oxide, cassiterite (SnO<sub>2</sub>). Tin does not occur in the free state. Simple reduction with carbon produces the metal. Tin has long been known, specimens being found in the Egyptian tombs.

It occurs close to, but above, hydrogen in the electrochemical series. It is not so active as zinc or iron, but is more active than copper or silver. Dilute acids act slowly with it. Concentrated hydrochloric acid forms stannous chloride and hydrogen, concentrated sulfuric acid oxidizes it to stannous sulfate (page 512), and nitric acid forms metastannic acid (H<sub>2</sub>SnO<sub>3</sub>). Tin burns at high temperatures, but is unchanged by air or water under ordinary conditions. It is attacked by fused alkalies. It forms bivalent and quadrivalent compounds. Both oxides and their hydroxides have acidic and basic properties. Stannous hydroxide is mainly a base, and stannic hydroxide is mainly an acid. The salts of stannic acid are called stannates.

Because of its inactivity, tin is used to plate sheet iron for roofing and tinware. Tin does not rust, but if scratched off, the iron rusts faster than if no tin were in contact with it (page 512). With galvanized iron, the zinc is attacked first. Tin is used in many alloys (page 497). Tin is recovered from tin cans and tin scrap by detinning with chlorine (page 514).

Lead. The principal ore of lead is the sulfide, galena, or galenite (PbS). Sulfide ores must be roasted before they can be reduced. The process can be so conducted that lead sulfide serves to reduce the oxides and sulfates formed by the roasting

(equations, page 515). Silver is obtained in the process, alloyed with the lead. Hard lead is first obtained, the hardness being due to impurities of arsenic, bismuth, antimony, copper, etc. These are burned to oxides, which float, by melting in an open furnace. The soft lead, thus obtained, contains silver. This is removed by the Parkes process (page 516).

Lead is a heavy metal, but not so heavy as gold, platinum, or mercury. It is just above hydrogen in the electrochemical series. It tarnishes, but is not acted upon to any extent by oxygen of the air. At high temperatures it burns. Nitric acid oxidizes it, but hydrochloric acid and sulfuric acid have little action on it because of the formation of insoluble lead salts. Weaker acids, like acetic, act with it. Lead is used in many alloys, in storage batteries, in pipes for plumbing, and in making white lead. Litharge (PbO), red lead (Pb<sub>3</sub>O<sub>4</sub>), and the peroxide (PbO<sub>2</sub>) are oxides of lead. Their uses are given on page 518.

Paints. Paints consist of three ingredients, body, vehicle, and pigment. White lead, basic lead carbonate (2PbCO<sub>3</sub>.Pb(OH)<sub>2</sub>) is the most commonly used body material. Zinc oxide is good. Barium sulfate and china clay are inferior substitutes, if sold as white lead. White lead is made from lead plates, acetic acid, and fermenting organic matter (page 519). The best vehicle is linseed oil. It drys by absorbing oxygen, and to make it dry quicker, it is boiled with oxides, which start the oxidation. The pigment is the coloring matter. This may be the body also, as lead chromate (yellow), but usually the pigment is a metallic oxide. Organic dyes are used in the form of lakes (pages 520 and 521).

Storage Batteries. There are two kinds of cells for storing electrical energy as chemical energy which can be liberated as electrical energy. The chemical action occurring when the cell is being charged is reversed when the cell is discharging current. The ordinary cell consists of lead plates covered with spongy lead at one pole and lead dioxide at the other when ready for use. The liquid is sulfuric acid solution. As it discharges, both plates become coated with lead sulfate (page 522). The other type (Edison cell) has one plate of iron and the other of nickelic oxide (Ni<sub>2</sub>O<sub>3</sub>). The solution is potassium hydroxide. The cell

operates by the nickel oxide being reduced to nickel hydroxide (Ni(OH)<sub>2</sub>) and the iron being oxidized to Fe(OH)<sub>2</sub>, which action delivers energy.

Manganese. This element forms a great variety of compounds. It has a valence from two to seven as shown by the oxides (page 525). Manganese dioxide, pyrolusite (MnO<sub>2</sub>), is the principal source of manganese. It is a good oxidizing agent. Manganese acts both as a positive and a negative element. As a positive element its manganous salts (page 525) are most important. Potassium permanganate (KMnO<sub>4</sub>) is the most common example of its acid-forming property. This compound is frequently used as an oxidizing agent (page 527) and is also an antiseptic and disinfectant.

Chromium. Chromium does not belong in the same group with manganese, but it acts as an acid-forming and base-forming element. It is hard to reduce from its ores, as is manganese. Chromium is trivalent and hexavalent. In its hexavalent form its acid properties are more noticeable. Chromic acid (H<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub>) and dichromic acid (H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) are unstable but form several well-known salts. Lead chromate (PbCrO<sub>4</sub>) is a yellow pigment; potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) is a common oxidizing agent (page 532).

Radioactivity. The term "radioactivity" is applied to the power which certain elements have of throwing off rays of a peculiar nature. These rays will pass through some substances opaque to light rays and affect a photographic plate. Also, they discharge a charged electroscope (page 536). Several elements and their compounds exhibit this property, uranium, radium, and thorium being among them. Radium shows the most marked radioactivity. This property was first discovered in connection with uranium compounds by Becquerel. The Curies observed that pitchblende, a mineral of uranium, was four times as active as uranium. This led them to believe that a more active radioactive substance existed as an impurity in pitchblende, and they succeeded in isolating radium from large quantities of pitchblende residues.

Radium. The element has chemical properties similar to those of barium, and it is placed after barium in that family. Radium

disintegrates, even though it is a well-defined element. In this disintegration, it forms helium and niton, both of which belong to Group O. Niton further decomposes, and it is thought that the final product is lead (page 542).

In these decompositions two kinds of particles are thrown off. The first kind, called *alpha rays*, consists of helium atoms charged positively; the second kind, called *beta rays*, consists of electrons, which are about  $\frac{1}{1800}$  as heavy as the hydrogen atom and are charged negatively. A third kind of radiation consists of waves in the ether and not of particles of matter. These are the *gamma rays* (page 538). Note the demonstration of these three kinds of rays in Fig. 208, page 539.

It is thought that radium is being formed from uranium. A great deal of energy is given off in the decomposition of radium. The rays from radium compounds disintegrate glass and water, produce severe burns upon the skin, and kill bacteria; they are used in treating some diseases, as cancer, and it is claimed that certain forms of cancer, if treated in the early states, can be cured.

The radium atom. The decomposition of radium suggests that the atoms of the elements must have a complex structure. It seems probable that the atoms are made up of a positive nucleus consisting of charged atoms of helium (possibly hydrogen also) closely packed and making up nearly all the mass of the atom and of negative electrons revolving about the nucleus. For radium this system is unstable, but for most of the elements the atom is stable. Gradually the atoms of radium are breaking up, the explosion resulting in vibrations that cause the gamma ray.

Rare elements. Some of the rare elements have an important use or two worth mentioning here. Thus thorium and cerium oxides are used in making gas mantles. Cerium compounds are used in photography and in mordants. Cerium oxalate is used in seasickness. An alloy of cerium and iron is used as a gas lighter. Titanium, vanadium, molybdenum, and tungsten are used in steel alloys. Tungsten is used for the filament in electric-light bulbs and is replacing platinum for electrical contacts. Vanadium compounds are used as catalytic agents, as photographic developers, as mordants, and in coloring glass. Titanium oxide is used to color

glass yellow and in electric-arc carbons to give a more efficient light. Selenium is a non-conductor in the light. Therefore, it has been used in automatic fire alarms. It imparts a red color to glass and enamels.

#### EXERCISES

- 1. State the source and give the metallurgy of tin.
- 2. Discuss the properties and the uses of tin.
- 3. Describe the metallurgy of lead.
- 4. What is the Parkes process?
- 5. Give the properties and the uses of lead.
- 6. Discuss the composition of paints.
- 7. Describe the manufacture of white lead.
- 8. Give names, formulas, and uses for the oxides of lead.
- 9. Explain the action of storage cells.
- 10. What is pyrolusite? What are its uses?
- 11. Explain the oxidizing action of potassium permanganate.
- 12. What is chrome yellow? What is its use? Write the equation for its formation.
  - 13. Explain the oxidizing action of potassium dichromate.
  - 14. What is radioactivity? Name three radioactive elements.
  - 15. How was radium discovered?
  - 16. What kinds of rays are emitted by radium?
  - 17. What are the uses of radium?
  - 18. Discuss the structure of the radium atom.
  - 19. Answer questions 1, 4, 5, 7, 12, and 13, page 523.
  - 20. Solve problems 8, 9, 11, and 14, page 523.

SEND EXERCISES FOR LESSONS XXI=XXV TO THE SCHOOL







